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The Raman Spectra of the Methyl Alcohols, CH_3OH, CH_3OD, and CH_2DOD *

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Measurements of the Raman spectra of CH_3OH, CH_3OD, and CH_2DOD, produced by the mercury lines at 2536 and 4358A units, are analyzed to yield a provisional assignment of the fundamental frequencies. The significance of the character of the OH and OD bands to the problem of internal rotation is discussed. A new approximation to a potential constant for the C−O bond is presented.

A PREVIOUS communication from this laboratory[1] presented data for the Raman spectra of CH_3OH and CH_3OD, excited by the mercury lines at 2536 and 4358A units. This paper presents additional lines and a few changes in position as the result of further examination of these spectra. The alcohol CH_2DOD has been prepared and subjected to a similar study.

CH_3OD was prepared by treating dry magnesium methylate with 99.8 percent D_2O and CH_2DOD was made by means of the reaction of diazomethane with D_2O in the presence of a small amount of D_2SO_4. Each of the alcohols was purified by fractional distillation.

A spiral mercury resonance lamp and a Hilger E3 spectrograph were used to obtain the shifts of the 2536 Hg line. For excitation by the 4358 Hg line, the radiation from four quartz mercury arcs in an apparatus similar to that of Anand[2] was passed through successive filters of cobalt thiocyanate, praeseodymium nitrate, and sodium nitrite, and the scattered light was photographed in a Gaertner spectrograph (f: 3.5).

The data are summarized in Table I, which includes estimates of intensity indicated by numbers from one to ten, and provisional assignments to modes of motion of the molecule. The two columns for CH_3OH include all of the frequencies shown in a table compiled by Voge[3] from his own measurements and those of Kohlrausch and of Wood, except for a broad band found by Voge in the region about 1450 cm^{-1}. This band was omitted from the table because no well-defined center was distinguishable from the line at 1464, but the indications are that it is connected with one of the fundamental vibrations. The CH_3OD spectrum is in good agreement with the data of Mizushima, Morino and Okamoto,[4] which appeared shortly after the publication of our first communication. Microphotometer tracings of the spectra listed in Table I are reproduced in Figs. 1 to 6. The correspondence between the figures and the tabulation is indicated at the head of the columns

* A part of the equipment used in this research was purchased with funds contributed by the National Research Council.

[1] Bates, Anderson and Halford, J. Chem. Phys. **4**, 535 (1936).

[2] Anand, J. Sci. Inst. **8**, 258 (1931).

[3] Voge, J. Chem. Phys. **2**, 264 (1934).

[4] Mizushima, Morino and Okamoto, Bull. Chem. Soc. Japan **11**, 699 (1936).

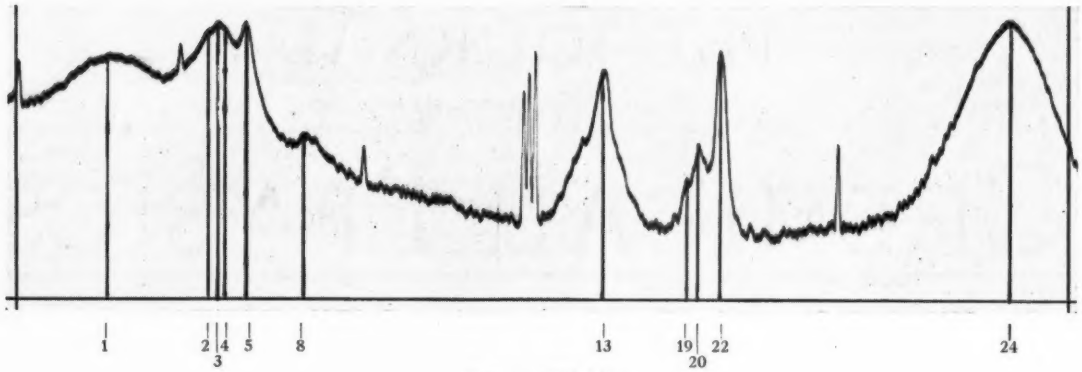

FIG. 1. CH_3OH.

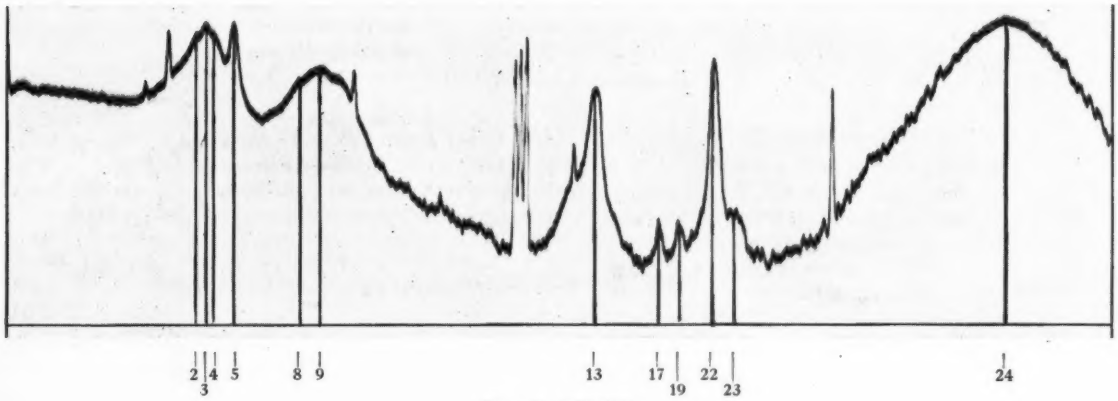

FIG. 2. CH_3OD

TABLE I.

No.	CH_3OH 2536 (Fig. 1)	CH_3OH 4358 (Fig. 4)	CH_3OD 2536 (Fig. 2)	CH_3OD 4358 (Fig. 5)	CH_2DOD 2536 (Fig. 3)	CH_2DOD 4358 (Fig. 6)	ASSIGNMENT
(1)	3382±100	3415±100					OH stretch
(2)	2992(4)	2982(6)	2989(4)	2986(6)	2974(4)	2985(6)	ν_2
(3)	2936(8)	2948(10)	2946(7)	2947(10)	2945(10)	2952(10)	ν_1, $2\nu_4$
(4)	2913(4)	2914(6)	2915(4)	2918(6)			$\nu_3+\nu_4$?
(5)	2835(10)	2839(10)	2836(10)	2836(10)	2885(10)	2880(8)	ν_1, $2\nu_4$
(6)					2835(3)		?
(7)					2686(3)		$2\nu_{4-2}$?
(8)	2588(1)		2591(1)				$\nu_3+\nu_6$?
(9)			2494±50	2494±50	2501±50	2500 } band	OD stretch
(10)						2383 }	
(11)					2237(?1)		$2\nu_6$?
(12)					2171(8)	2181(5)	ν_{2-2}
(13)	1464(5)	1451(4)	1464(5)	1465(4)	1462(6)	1477(3)	ν_3, ν_4
(14)		1370(?)		1370(?)			
(15)					1350(6)	1336(3)	ν_{4-2}
(16)					1301(6)		
(17)			1226(1)				?
(18)		1171(3)		1179(4)			4047 excitation
(19)	1153(1)		1153(1)	1154(2)			ν_6
(20)	1104(2)	1119(3)					OH bend
(21)		1056(4)		1071(4)			4047 excitation
(22)	1029(6)	1029(6)	1031(6)	1034(5)	1032(8)	1043(5)	ν_5
(23)			942(2)		881(2)	907(1)	OD bend
(24)	(2536A)		(2536A)		(2536A)		
(25)		(4358A)		(4358A)		(4358A)	

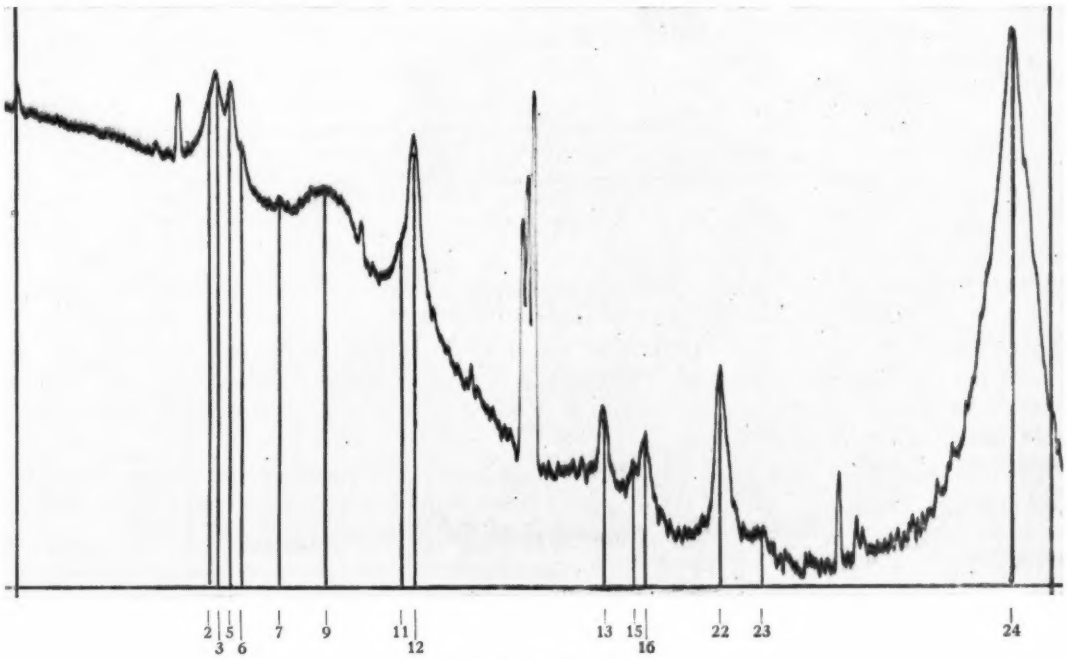

FIG. 3. CH_2DOD.

of the table. The numbers in the first column serve to identify the lines in the figures. Lines 2 and 4 do not show as well in the curves prepared for reproduction as in others which have been measured.

FUNDAMENTAL VIBRATIONS

Although in general the correlation of Raman shifts with fundamental vibrations is necessarily somewhat arbitrary and is therefore subject to uncertainty, it appears feasible from present knowledge of the magnitude of bond constants and of the vibrations of methyl compounds to make provisional assignments for methyl alcohol. For this purpose, reference to the work of Adel and Barker[5] on the methyl halides is of material assistance.

The notation adopted for the normal frequencies is taken from the scheme applied to the methyl halides by Dennison.[6] Its use in the methyl alcohol problem introduces the reasonable assumption that the dissymmetry occasioned by the position of the hydroxyl hydrogen atom will have negligible effect upon vibrations which belong primarily to the methyl and methoxy groups. In CH_3OH and CH_3OD, three motions (ν_1, ν_3 and ν_5) are described as parallel to the symmetry axis of the methoxy group and three (ν_2, ν_4 and ν_6) are perpendicular to the symmetry axis and doubly degenerate. CH_2DOD should show nine frequencies in these groups, three new ones occurring because of the splitting of the degenerate frequencies according to the orientation of their motion with respect to the plane of symmetry of the CH_2D group. These three deuterium frequencies are designated as ν_{2-2}, ν_{4-2}, and ν_{6-2}. Of the three additional degrees of freedom required to make up the total of twelve possessed by methyl alcohol as a hexatomic molecule, two should approximate, respectively, to bending and stretching of the OH or OD bond, while the third may be either free internal rotation or a torsional frequency, probably the latter.

The values of ν_1, ν_2 and ν_4, which are practically[7] invariant in methyl compounds, may be readily assigned. The line at 2987 cm^{-1} (CH_3OH and CH_3OD, 2980 for CH_2DOD) is ν_2, and the

[5] Adel and Barker, J. Chem. Phys. **2**, 627 (1934).
[6] Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[7] Sutherland and Dennison, Proc. Roy. Soc. **A864** (v148), 250 (1935).

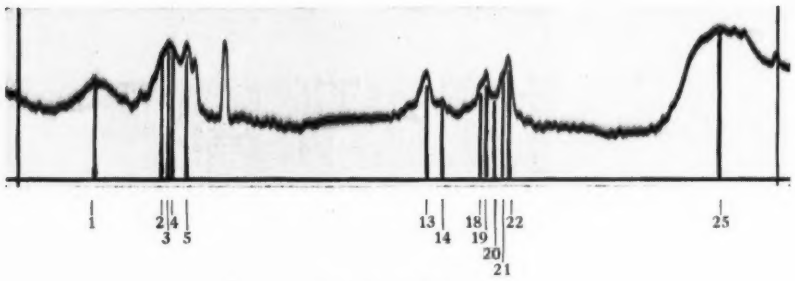

FIG. 4. CH_3OH.

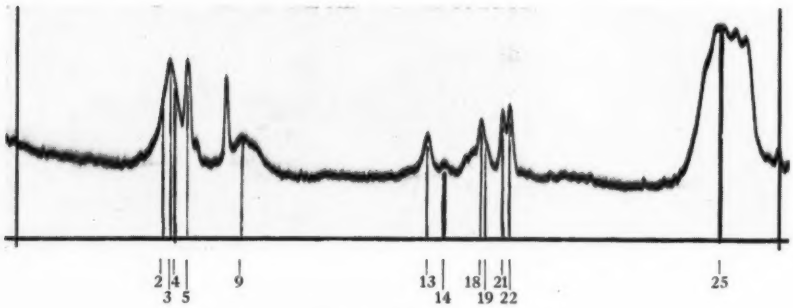

FIG. 5. CH_3OD.

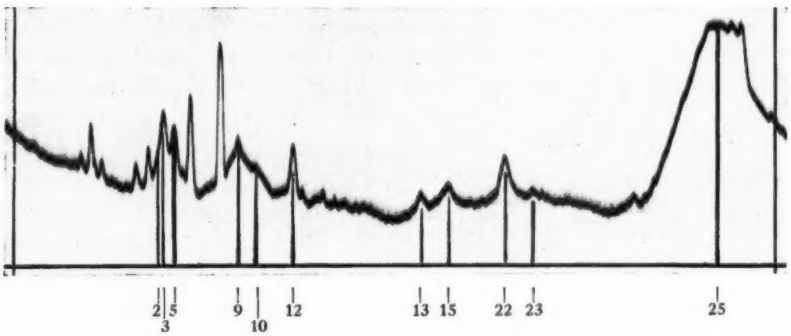

FIG. 6. CH_2DOD.

two strong high frequency lines (2835 and 2945 for CH_3OH and CH_3OD, 2883 and 2948 for CH_2DOD) arise from the interaction of ν_1 and $2\nu_4$ from which $\nu_1=2890$ and $\nu_4=1445$ may be taken as not far from correct for the symmetrical methoxy group. A correction for anharmonicity would bring ν_4 into coincidence with the weak band with center at 1452 reported by Voge, or with the relatively strong line at 1464. The weaker line at the lower frequency is the better assignment, because the perpendicular motions of this type of molecule tend to appear only weakly in the Raman effect. Consistency requires that $\nu_3=1464$, a conclusion that receives support from the occurrence of a line at 2915 cm^{-1} which must be either $\nu_3+\nu_4$ or $2\nu_3$, since $2\nu_4$ has already been accounted for. It follows that $\nu_3>\nu_4$ since $\nu_3+\nu_4$ (or $2\nu_3$) $>2\nu_4$.

The assignment $\nu_5=1031$ agrees with the generally accepted view that this is the C–O bond frequency. By comparison with the methyl halides, ν_6 should lie in the region between 1100 and 1300 cm^{-1}. The best selection appears to be the line at 1153 cm^{-1} which is observed as a shift of both the 2536 and the 4358 Hg lines for CH_3OH and CH_3OD. The deuterium line at

2176 cm^{-1} (columns 5 and 6) is undoubtedly ν_{2-2}; that at about 1340 cm^{-1} is probably ν_{4-2}. Neither ν_6 nor ν_{6-2} appears in the CH_2DOD spectrum.

The broad band with center at 3400 cm^{-1}, which has been reported by a number of previous workers for CH_3OH,[8] has been ascribed to the OH stretching motion. The corresponding OD band in the CH_3OD spectrum is narrower and more intense, and has its center at 2500 cm^{-1}, close to the position predicted from the assumption that the frequency ratio is determined by the masses of the protium and deuterium atoms. The similar band for CH_2DOD shows two intensity maxima, at 2500 and 2380 cm^{-1}, with the higher frequency maximum about twice as intense as the lower. This suggests that rotation of the OD group about the C−O bond is restricted, and that the two frequencies result from three more or less stable orientations of this group with respect to the plane of symmetry of the CH_2D radical. Two of these would be dynamically equivalent mirror images, accounting for the greater intensity of the one maximum. Unfortunately it is not possible to say with confidence that this is the correct explanation, because the effect of association in the liquid state cannot be eliminated, and the possibility of a splitting due to interaction of the OD frequency with a combination involving the new deuterium frequencies must be considered. It is interesting, however, that the production of sharp intensity maxima suggests the presence of vibrational states in the torsional motion. Further discussion of the character of the torsional motion is best deferred until data on the molecules containing the CHD_2 and CD_3 groups become available. The preparation of CHD_2OD and CD_3OD is now being studied in this laboratory.

In the original communication the CH_3OH line at about 1110 cm^{-1} was ascribed to the OH bending motion, primarily because it was not found in the CH_3OD spectrum. This line (20) appears distinctly only in the ultraviolet CH_3OH spectrum. Its acceptance as a line in the visible spectrum is based upon this fact together with the difference between the densitometer curves for CH_3OH and CH_3OD (Figs. 4 and 5). The same assignment has been made independently by Mizushima, Morino, and Okamoto. It should be recognized, however, that this conclusion may not be the correct one, since a line arising from association might be expected to behave in the same manner. What appears to be the corresponding OD line is found at 942 cm^{-1} on one of the CH_3OD plates and at 881 and 907 cm^{-1} on the CH_2DOD plates.

In addition to the assigned fundamentals and the high frequency combinations used in support of the assignments, a number of other lines are found in the spectra. Some of them may be accounted for as combinations, as shown in the last column of the table. The line at 2835 in the ultraviolet CH_2DOD spectrum is too high for the combination $\nu_3+\nu_{4-2}$, and may be a triple combination. There seems to be no good explanation for the lines at 1226 cm^{-1} (column 4), 1370 cm^{-1} (columns 3 and 5) and 1301 cm^{-1} (column 6), but their presence does not invalidate the selection of fundamentals if it is assumed that frequencies peculiar to the liquid state may appear. Furthermore, extra frequencies might appear in the CH_2DOD spectrum if two stable orientations of the OD group occur. The lines in the CH_3OH and CH_3OD spectra at about 1060 and 1175 cm^{-1} have been ascribed to excitation of the hydrogen frequencies by the 4047 Hg line, although they are somewhat more intense than would be predicted. Their absence from the CH_2DOD spectrum is explained by the fact that the exciting light was filtered through different filters resulting in a considerable decrease in intensity of the 4047 excitation.

Potential Constant of the C−O Bond

The frequency ν_5 has been used as the basis for a calculation of the Hooke's law constant of the C−O bond,[9] assuming that the methyl and hydroxyl groups act as point masses, and leads to the value $c=4.96(\times 10^5)$ dynes/cm. This assumption receives support from the calculations of Sutherland and Dennison, who have shown that when it is applied to the methyl halides it leads to a constant for the C−X bond

[8] Venkateswaran and Karl, Zeits. f. physik. Chemie **B1**, 466 (1928); Dadieu and Kohlrausch, Monatshefte **55**, 379 (1930); Medard, Comptes rendus **198**, 1407 (1934).

[9] Bonner, J. Chem. Phys. **5**, 293 (1937).

in substantial agreement with the result of a detailed analysis.

A minor refinement is suggested by the fact that ν_5 is the same, within the limits of error, for CH_3OH and CH_3OD, showing that the frequency does not depend upon the total mass of the hydroxyl group. A calculation using the mass of the oxygen atom instead of the OH group gives the result $c=4.74$.

A further approximation may now be made which takes into account the relative motion of the constituent atoms of the methyl group. Three constants may be calculated from ν_1, ν_3, and ν_5, if it is assumed for the purpose that these frequencies are analogous to the parallel frequencies of the methyl halide molecule. Sutherland and Dennison have expressed the frequencies in terms of the masses and four potential constants, making necessary the use of data from other methyl compounds in order to obtain a solution. It seems preferable here to employ a three-term potential function, producing a result which, although it may be less general, can more properly be said to yield the next approximation to the value of the C−O constant. Introducing the constants, k_1 for C−H stretching, k_2 for the sum of the expansions of the H−C−H and H−C−O angles, and c for C−O stretching, into the three relations gives the equations:

$$\lambda_1\lambda_3\lambda_5=\frac{M_1+M_2+3m}{m^2M_1M_2}k_1k_2c,$$

$$\lambda_1\lambda_3+\lambda_3\lambda_5+\lambda_5\lambda_1=\frac{c}{9}\left\{\frac{M_1+M_2+3m}{M_1M_2m}(k_1+8k_2)+\frac{M_1+M_2}{M_1M_2m}(8k_1+k_2)\right\}+\frac{M_2+3m}{M_2m^2}k_1k_2,$$

$$\lambda_1+\lambda_3+\lambda_5=\frac{M_2+3m}{9mM_2}(k_1+8k_2)+\frac{8k_1+k_2}{9m}+\frac{M_1+M_2}{M_1M_2}c.$$

λ has been substituted for $4\pi^2\nu^2$, M_1 is the mass of the oxygen atom, and M_2 and m are the masses of the carbon and hydrogen atoms. Simultaneous solution for the three constants yields two sets of values,

$$k_1=4.792,\quad k_2=0.684,\quad c=7.39$$

and

$$k_1=4.795,\quad k_2=0.875,\quad c=5.77,$$

of which the second set is the more reasonable physically. This new value for the C−O bond is not necessarily any nearer to the most representative one than is the constant 4.74 determined from ν_5 alone. The difference between the two, however, serves to show the magnitude of the uncertainty involved in the approximate calculations. It may be concluded, in any event, that considerable relative motion of the atoms of the methyl group is involved in the vibration ν_5.

The Structure of H_3, H_3^+, and of H_3^-. IV

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Frick Chemistry Laboratory, Princeton, New Jersey

(Received August 16, 1937)

In this paper, a direct calculation is made of the force constant for bending the nuclei in the triatomic hydrogen molecule, H_3, and in the ion, H_3^+, from a straight line. The neutral molecule has lower energy when the atoms are in a line rather than in neighboring triangular configurations. The opposite is true for the positive ion. The quantum-mechanical variational method is used together with the most general eigenfunctions which can be compounded from $1s$ hydrogen-like orbitals. The polar-homopolar composition of these eigenfunctions and the effective nuclear charge are varied simultaneously to give the lowest energy. For H_3, we obtain the force constant for bending, 15.88 kcal./radian^2, and the corresponding vibration frequency for bending, 3.26×10^{13} sec.$^{-1}$. These values agree well with those obtained by the semi-empirical scheme. The force constant for bending H_3^+ from a straight line is -15.41 kcal./radian^2. This negative value for the force constant indicates that the positive ion has lowest energy for triangular configurations, as predicted by Coulson. The energy of H_3^- is calculated for a linear symmetrical configuration. It is found that for reasonably small separations, H_3^- is unstable with respect to H_2+H^-. At large separations H^- is attracted to H_2 to form a loose cluster but a rough calculation of the equilibrium constant indicates that $\frac{\text{Concentration } H_3^-}{\text{Concentration } H^-}=0.2\times$pressure H_2 in atmospheres. Thus at the low pressures which are used in the mass spectrograph, H_3^- could not be detected.

IN the previous communications of this series,[1-3] only the linear configurations of H_3 and of H_3^+ were considered. In this paper, a direct calculation is made of the force constant for bending the linear H_3 and H_3^+. Furthermore, we calculate the energy of linear H_3^- and find that the reason why this ion has never been observed experimentally is that it is energetically unstable with respect to H_2+H^-. The force constant indicates that H_3 has a lower energy when the three nuclei are in a line as predicted by the first order perturbation method of London[4] and the semi-empirical scheme of Eyring and Polanyi.[5] This is quite different from the case of the triatomic hydrogen ion where the greatest binding energy is obtained for the triangular configurations. The reasons why H_3 should be linear and H_3^+ should be triangular have been discussed by Coulson.[6] He uses the method of molecular orbitals to develop the following argument: "In H_3^+, we are only concerned with two electrons, and thus, in the ground state, only one type of orbital is filled: the two electrons will have the same space wave function but opposed spins. We are to choose that configuration of the nuclei which gives this orbital greatest binding energy. If a, b, c (Fig. 1) is the linear molecule, then the lowest orbital will only represent resonance between $a-b$ and $b-c$; the resonance $a-c$ is too small to make any appreciable contribution to the bonding. But in the triangular model, all three resonances contribute, and we may therefore expect greater bonding. In passing to the neutral molecule H_3, however, a new type of orbital has to be introduced having a node along the dotted line of the figure; this gives a bonding $a-b$ and $b-c$ but a repulsion $a-c$; there is therefore a definite tendency for this molecule to open out into a flat triangle or a straight line." The negative ion, H_3^-, has a greater tendency to flatten out than the H_3 since it has two electrons in the lowest orbital and the other two in the orbital with the node. Unfortunately Coulson's

[1] J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. **4**, 121 (1936).
[2] J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. **4**, 130 (1936).
[3] J. Hirschfelder, H. Diamond, and H. Eyring, J. Chem. Phys. **5**, 695 (1937).
[4] F. London, Zeits. f. Physik **46**, 455 (1928); **50**, 24 (1928); *Probleme der Moderne Physik* (Hirzel & Co., 1928), p. 104.
[5] H. Eyring and M. Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).
[6] C. A. Coulson, Proc. Camb. Phil. Soc. **31(2)**, 244 (1935).

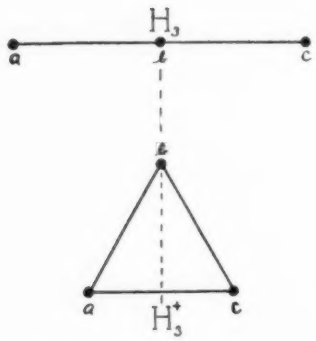

FIG. 1. H_3 is a linear molecule as shown by the upper diagram. H_3^+ is triangular as shown by the lower figure.

arguments do not constitute a rigorous proof; and it would be difficult to show, except by direct computations, that the increase in electronic binding energy more than compensates the hundreds of kilocalories increase in energy of nuclear repulsion when the H_3^+ is bent from a linear into a triangular configuration. Therefore, we determined to investigate the structure of the triatomic hydrogen molecule and ions using the variational method and the best eigenfunctions compounded from 1s hydrogen-like orbitals.

BENDING VIBRATION FREQUENCY FOR H_3

In order to obtain the vibration frequency for bending H_3 from the straight line, it is first necessary to compute the second derivative of the energy with the bending angle, θ (Fig. 2). This energy for various types of approximations has been expressed as an explicit function of a number of individual integrals.[7] The principal difficulty in this work was in obtaining the angle dependence of these integrals. Details of the mathematical analysis and the results are given in the appendix. It is a simple matter to substitute these integrals and their angle derivatives into the expressions for energy. The calculation of the energy for the Heitler-London[8] type of approximation will serve to illustrate the method which we employ. Consider the symmetrical configuration of the three hydrogen atoms such that the distance between nuclei a and b and between b and c is equal to R Bohr radii while the separation between nuclei a and c is equal to R_{ac} Bohr radii. We shall designate Bohr radii by the symbol a_0. Fig. 2 shows this arrangement of the nuclei. From our previous work,[1, 7] the energy of the H_3 for the Heitler-London approximation is:

$$E = H/S, \tag{1}$$

where $$S = 1 + I^2(R) - I^2(R_{ac}) - I^2(R)I(R_{ac}) \tag{2}$$

and

$$\begin{aligned} Ha_0/e^2 = {} & S(2/R + 1/R_{ac} - 1.5) \\ & - 2G(R)[1 - I^2(R_{ac})] \\ & - [G(R) + G(R_{ac})][2 + I^2(R)] \\ & + [K(b, ac) + J(R_{ac})][2I(R_{ac}) + I^2(R)] \\ & - 2[K(a, bc) + J(R)][I(R) - I(R)I(R_{ac})] \\ & + 2L(aa, bb) + L(aa, cc) - L(ac, ac) + L(ab, ab) \\ & - 2I(R_{ac})L(bb, ac) + 2I(R)L(aa, bc) \\ & - 2I(R)L(ab, ac) - I(R_{ac})L(ab, bc). \end{aligned} \tag{3}$$

Here we have used the Rosen[9] notation:

$$\begin{aligned} I(R) &= \pi^{-1} \int \exp(-r_{a1} - r_{b1}) d\tau_1, \\ I(R_{ac}) &= \pi^{-1} \int \exp(-r_{a1} - r_{c1}) d\tau_1, \\ G(R) &= \pi^{-1} \int (r_{b1})^{-1} \exp(-2r_{a1}) d\tau_1, \\ G(R_{ac}) &= \pi^{-1} \int (r_{c1})^{-1} \exp(-2r_{a1}) d\tau_1, \\ J(R) &= \pi^{-1} \int (r_{b1})^{-1} \exp(-r_{a1} - r_{b1}) d\tau_1, \\ J(R_{ac}) &= \pi^{-1} \int (r_{a1})^{-1} \exp(-r_{a1} - r_{c1}) d\tau_1, \\ K(a, bc) &= \pi^{-1} \int (r_{a1})^{-1} \exp(-r_{b1} - r_{c1}) d\tau_1, \\ K(b, ac) &= \pi^{-1} \int (r_{b1})^{-1} \exp(-r_{a1} - r_{c1}) d\tau_1, \\ L(\alpha\beta, \gamma\delta) &= \pi^{-2} \int\int (r_{12})^{-1} \\ &\quad \times \exp(-r_{\alpha 1} - r_{\beta 1} - r_{\gamma 2} - r_{\delta 2}) d\tau_1 d\tau_2, \end{aligned} \tag{4}$$

where α, β, γ, δ may stand for the position of the

[7] J. O. Hirschfelder, Dissertation, Princeton University (1935).

[8] Heitler and London, Zeits. f. Physik **44**, 455 (1927).

[9] N. Rosen, Phys. Rev. **38**, 255 (1931); **38**, 2099 (1931).

nuclei a, b, c. The second derivative of the energy, E, with respect to the bending angle, θ, is

$$\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0}=\frac{1}{S}\left(\frac{\partial^2 H}{\partial\theta^2}\right)_{\theta=0}-\frac{H}{S^2}\left(\frac{\partial^2 S}{\partial\theta^2}\right)_{\theta=0}. \quad (5)$$

All of the integrals which are functions of $R_{ac}\equiv 2R\cos(\theta/2)$ as well as the integrals: $K(b, ac)$, $K(a, bc)$, $L(aa, cc)$, $L(ac, ac)$, $L(bb, ac)$, $L(aa, bc)$, $L(ab, ac)$, and $L(ab, bc)$ are functions of θ. The second derivatives of these integrals with respect to θ are discussed in the appendix. When we substitute the values of these derivatives for the best separation of the nuclei, $R=2.0a_0$, into (5), we obtain:

$$\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0}=14.75 \text{ kcal./radian}^2=1.018\times10^{-12} \text{ ergs/radian}^2. \quad (6)$$

Since $(\partial^2 E/\partial\theta^2)_{\theta=0}$ is positive, H_3 is more stable in the linear configuration than when the nuclei are bent from the line. The vibration frequency for bending, ν_θ, corresponding to this force constant is[7]

$$\nu_\theta=(\pi R)^{-1}\left(\frac{3}{2m_H}\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0}\right)^{\frac{1}{2}}=2.89\times10^{13} \quad (7)$$

and $$h\nu_\theta=2.74 \text{ kcal.}$$

A better approximation to the energy of the triatomic molecule is obtained by varying the effective nuclear charge, z, or the screening constant, $z-1$, so as to obtain the lowest energy. This variation leads to the Wang[10] type of approximation and can be carried out very easily without the calculation of any additional integrals. When the effective nuclear charge is introduced, the energy becomes[1, 7]

$$E_z=zE_{z=1}+z(z-1)A/S, \quad (8)$$

where

$$A=3/2-\tfrac{1}{2}I^2(R)+2J(R)I(R)+\tfrac{1}{2}I^2(R_{ac})-2I(R_{ac})J(R_{ac})+(3/2)I(R_{ac})I^2(R)-I^2(R)J(R_{ac})-2I(R)I(R_{ac})J(R). \quad (9)$$

Here R and R_{ac} now stand for z times the actual nuclear separations. Taking the second derivative of (8) with respect to θ and using the best value of z ($z=1.05864$) for the best separation between nuclei, $r_{ab}=R/z=1.889a_0$:

$$\left(\frac{\partial^2 E_z}{\partial\theta^2}\right)_{\theta=0}=18.04 \text{ kcal./rad.}^2=1.245\times10^{-12} \text{ ergs/rad.}^2.$$

From which it follows that

$$\nu_{\theta \text{ Wang App.}}=3.370\times10^{13}$$

and $$h\nu_{\theta \text{ Wang App.}}=3.20 \text{ kcal.}$$

The binding energy becomes a very complicated function of the individual integrals when the eigenfunction is taken to be the best linear combination of the homopolar function and the three polar states which are antisymmetric with respect to a permutation of the nuclei a and c. However, the procedure for computing the bending frequency remains the same as for the simpler Heitler-London approximation. Thus we find for the Heitler-London plus-polar states approximation:

$$\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0}=11.11\frac{\text{kcal.}}{\text{rad.}^2}, \quad \nu_\theta=2.508\times10^{13}, \quad h\nu_\theta=2.38 \text{ kcal.}$$

Now varying the effective nuclear charge to form the Wang plus-polar states approximation:

$$\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0}=15.88\frac{\text{kcal.}}{\text{rad.}^2}, \quad \nu_\theta=3.26\times10^{13}, \quad h\nu_\theta=3.09 \text{ kcal.}$$

Thus in all four approximations, the energy of H_3 is lower for the linear than for the neighboring triangular configurations. However we cannot rule out the possibility of the energy of H_3 having more than one minimum when it is plotted as a function of θ. A direct calculation of the energy

FIG. 2. θ is the angle of bending of the molecule from the straight line. The separations between nuclei a and b and between nuclei b and c are equal to Ra_0 where a_0 is the length of the Bohr radius.

[10] S. C. Wang, Phys. Rev. **31**, 579 (1928).

TABLE I. *Bending frequencies for the vibration of H_3 calculated in a number of different ways.*

	$(\partial^2 E/\partial\theta^2)_{\theta=0}$	ν_θ	$h\nu_\theta$	E	r_{ab}
Heitler-London Approx.	14.75 $\frac{\text{kcal.}}{\text{rad.}^2}$	2.89×10^{13} sec.$^{-1}$	2.74 kcal.	−53.1 kcal.	$2.0a_0$
Wang Approx.	18.04	3.37	3.20	−56.2	1.89
H. L. Plus-Polar States Approx.	11.11	2.51	2.38	−60.4	2.00
Wang Plus-Polar States Approx.	15.88	3.26	3.09	−67.1	1.84
Semi-Empirical (20% Coulombic)	10.93	2.70	2.56	−102.2	1.84

for the equilateral triangular configuration will be made as soon as possible.

Beside the ground state of the H_3 molecule which is antisymmetric with respect to a permutation of the nuclei a and c, there is an excited state which is symmetric with respect to such a permutation. If we consider only the homopolar eigenfunctions, this excited state corresponds to a bond between the widely separated nuclei a and c. The energy of this state is such as to make the atoms repel each other at all separations. It is interesting to find that such a repulsive state has its lowest energy for the linear configuration and its bending vibration frequency is similar to that for the ground state. We calculate: (repulsive state, Heitler-London approximation)

$$\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0}=10.00\frac{\text{kcal.}}{\text{rad.}^2},\quad \nu_\theta=2.38\times10^{13},\quad h\nu_\theta=2.26\text{ kcal.}$$

The results which we have obtained for the triatomic molecule by the variational method are in excellent agreement with those calculated by the semi-empirical scheme of Eyring and his co-workers[11] In that treatment, the energy of the symmetrical H_3 is

$$E=3E_H+(1+n)w(r_{ab})-(1-2n)w(r_{ac}). \quad (10)$$

Here $E_H=-\frac{1}{2}e^2/a_0$ is the energy of the separated hydrogen atoms, $w(r_{ab})$ and $w(r_{ac})$ are the Morse curve potential energies for normal hydrogen molecules in which the nuclei are separated a distance r_{ab} and r_{ac} respectively, i.e.

$$w(r_{ab})=D'[\exp(-2a(r_{ab}-r_0))-2\exp(-a(r_{ab}-r_0))], \quad (11)$$

where D' is the energy of dissociation of the normal H_2 plus the zero-point energy, r_0 is the equilibrium separation for the diatomic molecule, and a is a constant determining the curvature of the potential energy. For H_2: $D'=108.8$ kcal., $a=1.94\times10^8$ cm^{-1}, $r_0=0.75\times10^{-8}$ cm. In Eq. (10), n is the so-called fraction of Coulombic energy. According to the first-order perturbation theory, the total binding energy, $w(r_{ab})$, of a diatomic molecule is the sum of a Coulombic part and another term, the exchange energy, which is a function of the electronic binding state. In the Eyring scheme, the Coulombic energy is $nw(r_{ab})$ and for best results n is usually taken to be 0.20. The principal justification of the semi-empirical scheme arises from the agreement which is obtained with the experimentally measured activation energy for a large number of cases. From Eq. (10) it follows that

$$\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0}=-(1-2n)\left(\frac{\partial^2 w(r_{ac})}{\partial\theta^2}\right)_{\theta=0}=(1-2n)D'ar_{ab}[\exp(-a(r_{ac}-r_0))-\exp(-2a(r_{ac}-r_0))]. \quad (12)$$

Taking $n=0.20$ and $r_{ab}=1.84a_0$, we obtain:

$$\left(\frac{\partial^2 E}{\partial\theta^2}\right)_{\theta=0}=10.93\frac{\text{kcal.}}{\text{rad.}^2},\quad \nu_\theta=2.70\times10^{13},\quad h\nu_\theta=2.56\text{ kcal.}$$

Table I shows all of the results which are obtained from both the semi-empirical and the variational method calculations. The agreement is surprisingly good and gives a further justification for the use of the semi-empirical scheme.

FORCE CONSTANT FOR BENDING H_3^+

The force constant for bending H_3^+ from the straight line is calculated in exactly the same

[11] See, for example, J. Hirschfelder, H. Eyring, and B. Topley, J. Chem. Phys. 4, 170 (1936) or Appendices 3 and 4 in the dissertation of one of us (J.O.H., reference 7).

manner by the variational method as for the case of the neutral molecule. The same integrals occur in both problems and these may be substituted into the explicit expressions which we have derived for the energy.[2, 7] Since the polar states are of great importance in the charge distribution of H_3^+, we consider immediately the Heitler-London plus-polar states and the Wang plus-polar states approximations. In the former case,

$$\left(\frac{\partial^2 E}{\partial \theta^2}\right)_{\theta=0} = -9.96 \frac{\text{kcal.}}{\text{rad.}^2}$$

and in the latter, $-15.41 \dfrac{\text{kcal.}}{\text{rad.}^2}$ (see Table II).

Since the force constant is negative for both approximations, the triatomic ion is more stable when the nuclei are in a triangle than when they form a straight line. This result, as was mentioned previously, is in accord with the expectations of Coulson.[6] A direct calculation of the energy of H_3^+ for the equilateral triangular configuration will be made as soon as the necessary integrals are evaluated.

From the variational method calculations of the energy required to bend H_3 and H_3^+ through an infinitesimal angle from the straight line, we see that H_3 has the lowest energy for the linear and H_3^+ for the triangular configurations. Thus it is energetically easier for a hydrogen atom to approach a hydrogen molecule along the line of nuclei; but the most favorable approach of a proton to a hydrogen molecule is along a path perpendicular to this line of nuclei.

The Energy of H_3^-

At large separations, an ion is attracted to a neutral molecule by ionic polarization forces. When a proton, H^+, approaches a hydrogen molecule, H_2, a stable ion, H_3^+, is formed. The question arises as to whether when H^- approaches H_2, a stable molecular ion H_3^- is formed. Ions of the type X_3^- are observed for the halogens in the mass spectrograph,[12] but H_3^- has never been discovered. In a previous communication[13] it was shown that the diatomic hydrogen ion, H_2^- is unstable. In this treatment we treat H_3^- by means of the quantum mechanical variational method and we find that the energy corresponds to a strong repulsion between H^- and H_2 at small separations. The minimum energy for H_2+H^-, just as for $H+H^-$, is of the order of a few calories binding and occurs for large separations.

The energy of H_3^- is calculated using the most general linear combination of states which can be formed from $1s$ hydrogen-like orbitals. We consider the symmetrical linear configuration for $r_{ab}=r_{bc}=2.0a_0/z$. (See Fig. 2 where $\theta=0$.) Here z is the effective nuclear charge in the eigenfunctions, as in the other examples which we have just considered. Since the Hamiltonian is symmetrical with respect to nuclei a and c, it follows that those eigenfunctions which are symmetric with respect to a permutation of a and c are noncombining or orthogonal with respect to those that are antisymmetric in this sense. There are four symmetric eigenfunctions which can be formed from the $1s$ hydrogen-like orbitals:

$$\begin{aligned}
\chi_1 &= \begin{pmatrix} a & a & b & c \\ \alpha & \beta & \alpha & \beta \end{pmatrix} - \begin{pmatrix} a & a & b & c \\ \alpha & \beta & \beta & \alpha \end{pmatrix} \\
&\quad + \begin{pmatrix} c & c & a & b \\ \alpha & \beta & \alpha & \beta \end{pmatrix} - \begin{pmatrix} c & c & a & b \\ \alpha & \beta & \beta & \alpha \end{pmatrix}, \\
\chi_2 &= \begin{pmatrix} b & b & a & c \\ \alpha & \beta & \alpha & \beta \end{pmatrix} - \begin{pmatrix} b & b & a & c \\ \alpha & \beta & \beta & \alpha \end{pmatrix}, \\
\chi_3 &= \begin{pmatrix} a & a & b & b \\ \alpha & \beta & \alpha & \beta \end{pmatrix} + \begin{pmatrix} c & c & b & b \\ \alpha & \beta & \alpha & \beta \end{pmatrix}, \\
\chi_4 &= \begin{pmatrix} a & a & c & c \\ \alpha & \beta & \alpha & \beta \end{pmatrix}.
\end{aligned} \tag{13}$$

Here the quantities in parenthesis indicate the usual Slater determinants and α and β are the two eigenfunctions corresponding to the eigenvalues $h/4\pi$ and $-h/4\pi$ for the z component of electron spin. The state χ_1 corresponds to a resonance between the configuration with two electrons on a and the other two electrons forming the bond

TABLE II. *Force constant for bending H_3^+ from a straight line.*

	$(\partial^2 E/\partial\theta^2)_{\theta=0}$	$E-2E_H$	r_{ab}
Heitler-London Plus-Polar States Approx.	$-9.96 \frac{\text{kcal.}}{\text{rad.}^2}$	−108.6 kcal.	2.00 a_0
Wang Plus-Polar States Approx.	−15.41	−155.4	1.52

[12] For example I_3^-, Hogness and Harkness, Phys. Rev. **32**, 784 (1928).
[13] H. Eyring, J. O. Hirschfelder and H. S. Taylor, J. Chem. Phys. **4**, 479 (1936).

TABLE III. *Energy of H_3^-. These energies are given with reference to three hydrogen atoms and an electron all infinitely far apart.* $r_{ab}=r_{bc}=2.0\ a_0/z$

	Energy H_3^- − 3 Energy H	
Symmetric States (symmetric with respect to an interchange of a and c)		
Heitler-London Approx.	−26.2	kcal./mole
Wang Approximation	−41.1	($z=0.89$)
H.L. Plus-Polar Approx.	−30.3	
Wang Plus-Polar Approx.	−43.7	($z=0.89$)
Antisymmetric States		
Heitler-London Approx.	+300	

$b-c$ and the configuration with two electrons on c and the other two forming the bond $a-b$. The state χ_2 corresponds to two electrons on b one on a and one on c forming the bonds $a-b$ and $b-c$. The states χ_3 and χ_4 are pure polar states. There are two antisymmetrical eigenfunctions:

$$\chi_5=\begin{pmatrix}a&a&b&c\\ \alpha&\beta&\alpha&\beta\end{pmatrix}-\begin{pmatrix}a&a&b&c\\ \alpha&\beta&\beta&\alpha\end{pmatrix}-\begin{pmatrix}c&c&a&b\\ \alpha&\beta&\alpha&\beta\end{pmatrix}+\begin{pmatrix}c&c&a&b\\ \alpha&\beta&\beta&\alpha\end{pmatrix}, \quad (14)$$

$$\chi_6=\begin{pmatrix}a&a&b&b\\ \alpha&\beta&\alpha&\beta\end{pmatrix}-\begin{pmatrix}c&c&b&b\\ \alpha&\beta&\alpha&\beta\end{pmatrix}.$$

The symmetrical states give the lowest energy. This is to be expected from the molecular orbital point of view. The lowest molecular orbital for an electron in the field of three hydrogen nuclei is symmetrical in a and c. The orbital corresponding to the first excited state has a node through b and is antisymmetrical with respect to a permutation of a and c. The positive ion, H_3^+, has two electrons in the lowest orbital and is therefore symmetrical in a and c. The neutral molecule has one electron in the excited state and is antisymmetrical. The negative ion has two electrons in the excited state and is symmetric since the product of the two antisymmetrical functions is symmetrical.

Taking $\Psi=A_1\chi_1+A_2\chi_2$ as the eigenfunction and varying the constants A_1 and A_2 so as to get the lowest energy, we get a Heitler-London type of approximation. By varying the effective nuclear charge, z, simultaneously with the A's, we obtain a Wang type of approximation. The inclusion of the polar states does not affect the results appreciably. Table III shows the values which we obtain. The greatest binding energy for the three hydrogen atoms and the electron in the configuration which we consider is 43.7 kcal. Since an electron is bound to a hydrogen atom in H^- with 16.5 kcal. and the two hydrogen atoms in H_2 are held together by 92.2 kcal. to the approximation of our calculations, we see that our configuration of H_3^- will dissociate into H_2+H^- giving off an energy $16.5+92.2-43.7=65.0$ kcal. From this result it is apparent that H_3^- is analogous to H_2^-. At large separations, H^- is attracted to H_2; at small separations it is repelled. For some large separation there will be a minimum for the energy of the system with possibly a few discrete vibrational and rotational states corresponding to a stable H_3^- molecule. Entropy considerations will favor the decomposition of H_3^- and we can make a rough calculation or estimate of the ratio of H_3^- to H^- which should be present at equilibrium on the assumption that H_3^- is a loose cluster with the H^- held to the H_2 by ionic-polarization forces. This calculation is identical with the one which has already been given for other clusters in hydrogen.[13] Using Eq. (12) of that reference we see that if the H^- is separated a distance of 2.8 angstrom from the H_2 at room temperature.[14]

$$\frac{\text{Concentration } H_3^-}{\text{Concentration } H^-}=0.2\times\text{pressure } H_2 \text{ in atmospheres.} \quad (15)$$

Thus under the conditions of the mass spectrograph, i.e., pressures under a thousandth of an atmosphere, it would be extremely difficult to detect H_3^- which would be present in less than 1/5000 the concentration of the H^-. The above estimate should be accurate as to order of magnitude.

APPENDIX

Integrals

The principal difficulty in obtaining the energy of a molecule by the variational method is due to the complicated nature of the integrals which arise when even a simple form for the charge distribution is assumed. In all of the calculations which we have made for H_3 and H_3^+, the eigenfunctions have been compounded from $1s$ hydrogen-like orbitals. The energy is then expressed in terms

[14] The assumption is made that the frequency of vibration of the H_2 with respect to H^- is 100 cm^{-1} which is a reasonable magnitude. If some other value were taken for this frequency, the results would not be appreciably changed.

of the I, G, J, K, and L integrals defined in Eq. (4). All of these integrals except the four three-center multiple exchange integrals: $L(aa, bc)$, $L(bb, ac)$, $L(ab, ac)$, and $L(ab, bc)$ are known for all configurations of the nuclei and there is little difficulty in obtaining the second derivatives of these integrals with respect to θ. Thus if we designate the operator $(\partial^2/\partial\theta^2)_{\theta=0}$ by the superscript $''$:

$$
\begin{aligned}
I''(R_{ac}) &= (1/3)(R^2+2R^3)\exp(-2R),\\
J''(R_{ac}) &= R^2\exp(-2R),\\
G''(R_{ac}) &= \tfrac{1}{4}G(2R)-(R+\tfrac{1}{4})\exp(-4R),\\
L''(aa, ac) &= (1/16)[\{16R^2-7R+(5/4)+(5/8R)\}\\
&\quad\times\exp(-2R)-\{3R+(15/4)\\
&\quad+(5/8R)\}\exp(-6R)],\\
L''(aa, cc) &= \tfrac{1}{4}L(aa, cc)-[(5/32)+(5/8)R+R^2\\
&\quad+(2/3)R^3]\exp(-4R),\\
L''(ac, ac) &= \tfrac{1}{4}L(ac, ac)+(2/5)(R+2R^2)\\
&\quad\times\{C+\log(2R)\}I(2R)\exp(-2R)\\
&\quad+(2/5)(R-2R^2)F(2R)Ei(-8R)\exp(+2R)\\
&\quad-(2/5)(2R-(16/3)R^3)Ei(-4R)\\
&\quad-[(5/32)+(5/8)R+\tfrac{1}{2}R^2+(28/15)R^3\\
&\quad+(8/15)R^4]\exp(-4R),\\
K''(c, ab) &= -2K(c, ab)+(2R)^{-1}\\
&\quad\times[3I(R)-(3+5R+R^2)\exp(-3R)],\\
K''(b, ac) &= \tfrac{1}{2}K(b, ac)+\tfrac{1}{4}R(1+2R)(C+\log(4R))\\
&\quad\times\exp(-2R)-\tfrac{1}{4}R(1-2R)\exp(+2R)Ei(-4R)\\
&\quad-(\tfrac{1}{2}+R+R^2)\exp(-2R).
\end{aligned}
\tag{16}
$$

In these equations, $Ei(-x)$ is the integral logarithm[18] defined by the relation $Ei(-x)=-\int_x^\infty x^{-1}\exp(-x)dx$. C is the transcendental $0.577215665\cdots$. The other new function introduced is

$$F(2R)=(1-2R+(4/3)R^2)\exp(+2R).$$

The computation of the second derivatives of the three-center multiple exchange integrals is much more difficult. Each of these involve θ through the factor $\exp(-r_{c2})$ in the integrand. If we use the ellipsoidal coordinates with a and b as foci:

$$\lambda_2=(r_{a2}+r_{b2})/R,\quad \mu_2=(r_{a2}-r_{b2})/R,\quad \phi_2 \tag{17}$$

it follows that

$$
\begin{aligned}
r_{c2} &= \tfrac{1}{2}R[(\lambda_2^2+\mu_2^2-6\mu_2\lambda_2+8)-8\cos\phi\cos(\theta/2)\\
&\quad\times(1-\cos^2(\theta/2))^{\frac{1}{2}}((\lambda_2^2-1)(1-\mu_2^2))^{\frac{1}{2}}\\
&\quad+8(1-\cos^2(\theta/2))(\mu_2\lambda_2-1)]^{\frac{1}{2}}.
\end{aligned}
\tag{18}
$$

The form of r_{c2} is of such a complicated nature that it would be necessary to carry out the integrations over λ_2, μ_2, ϕ_2 numerically for the three-center multiple exchange integrals whenever θ is not zero. From (18) it may be shown that:

$$
\begin{aligned}
\left(\frac{\partial^2}{\partial\theta^2}\exp(-r_{c2})\right)_{\theta=0} &= \exp(-r_{c2})[\tfrac{1}{4}R^4(r_{c2}^{-2}+r_{c2}^{-3})\\
&\quad\times(\lambda_2^2-1)(1-\mu_2^2)\cos^2\phi_2-\tfrac{1}{2}R^2r_{c2}^{-1}(\mu_2\lambda_2-1)].
\end{aligned}
\tag{19}
$$

For this case, r_{c2} is not a function of ϕ_2, since θ in (18) is set equal to zero.

The four three-center multiple exchange integrals are

$$
\begin{aligned}
L(aa, bc) &= \pi^{-2}\int\int(r_{12})^{-1}\exp(-2r_{a1}-r_{b2}-r_{c2})d\tau_2d\tau_1,\\
L(bb, ac) &= \pi^{-2}\int\int(r_{12})^{-1}\exp(-2r_{b1}-r_{a2}-r_{c2})d\tau_2d\tau_1,\\
L(ab, ac) &= \pi^{-2}\int\int(r_{12})^{-1}\exp(-r_{a1}-r_{b1}-r_{a2}-r_{c2})d\tau_2d\tau_1,\\
L(ab, bc) &= \pi^{-2}\int\int(r_{12})^{-1}\exp(-r_{a1}-r_{b1}-r_{a2}-r_{c2})d\tau_2d\tau_1.
\end{aligned}
\tag{20}
$$

In each of these cases the integration can be carried out over the coordinates of electron 1 regardless of the position of the nuclei. It will be noticed that the only dependence of these integrals on θ is through the $\exp(-r_{c2})$ factor in the integrand, so that this integration over the first electron is independent of θ. Remembering that

$$
\begin{aligned}
G(r_{a2}) &= \pi^{-1}\int(r_{12})^{-1}\exp(-2r_{a1})d\tau_1=(r_{a2})^{-1}\\
&\quad-(1+(r_{a2})^{-1})\exp(-2r_{a2}),\\
G(r_{b2}) &= \pi^{-1}\int(r_{12})^{-1}\exp(-2r_{b1})d\tau_1\\
&= r_{b2}^{-1}-(1+r_{b2}^{-1})\exp(-2r_{b2}),\\
K(2, ab) &= \pi^{-1}\int(r_{12})^{-1}\exp(-r_{a1}-r_{b1})d\tau_1,
\end{aligned}
\tag{21}
$$

the three-center multiple exchange integrals become:

$$
\begin{aligned}
L(aa, bc) &= K(a, bc)-T(a, bc),\\
T(a, bc) &= \pi^{-1}\int(1+r_{a2}^{-1})\exp(-2r_{a2}-r_{b2}-r_{c2})d\tau_2,\\
L(bb, ac) &= K(b, ac)-T(b, ac),\\
T(b, ac) &= \pi^{-1}\int(1+r_{b2}^{-1})\exp(-2r_{b2}-r_{a2}-r_{c2})d\tau_2,\\
L(ab, ac) &= \pi^{-1}\int K(2, ab)\exp(-r_{a2}-r_{c2})d\tau_2,\\
L(ab, bc) &= \pi^{-1}\int K(2, ab)\exp(-r_{b2}-r_{c2})d\tau_2.
\end{aligned}
\tag{22}
$$

It is again convenient to use the ellipsoidal coordinates (17) in which the volume element is

$$d\tau_2=(R^3/8)d\lambda_2d\mu_2d\phi_2(\lambda_2^2-\mu_2^2).$$

Now differentiating the integrands with respect to θ and making use of (19), we obtain:

$$
\begin{aligned}
T''(a, bc) &= \tfrac{1}{4}R^3\int_1^\infty\int_{-1}^1 P(1+(\tfrac{1}{2}R(\lambda_2+\mu_2))^{-1})\\
&\quad\times\exp(-\tfrac{1}{2}R(3\lambda_2+\mu_2))d\mu_2d\lambda_2,\\
T''(b, ac) &= \tfrac{1}{4}R^3\int_1^\infty\int_{-1}^1 P(1+(\tfrac{1}{2}R(\lambda_2-\mu_2))^{-1})\\
&\quad\times\exp(-\tfrac{1}{2}R(3\lambda_2-\mu_2))d\mu_2d\lambda_2,\\
L''(ab, ac) &= \tfrac{1}{4}R^3\int_1^\infty\int_{-1}^1 PK(2, ab)\\
&\quad\times\exp(-\tfrac{1}{2}R(\lambda_2+\mu_2))d\mu_2d\lambda_2,\\
L''(ab, bc) &= \tfrac{1}{4}R^3\int_1^\infty\int_{-1}^1 PK(2, ab)\\
&\quad\times\exp(-\tfrac{1}{2}R(\lambda_2-\mu_2))d\mu_2d\lambda_2,
\end{aligned}
\tag{23}
$$

where

$$
\begin{aligned}
P &= (2\pi)^{-1}(\lambda_2^2-\mu_2^2)\int_0^{2\pi}\left(\frac{\partial^2}{\partial\theta^2}\exp(-r_{c2})\right)_{\theta=0}d\phi_2\\
&= \exp(-r_{c2})(\lambda_2^2-\mu_2^2)[(R^4/8)(r_{c2}^{-2}+r_{c2}^{-3})\\
&\quad\times(\lambda_2^2-1)(1-\mu_2^2)-\tfrac{1}{2}R^2r_{c2}^{-1}(\mu_2\lambda_2-1)].
\end{aligned}
\tag{24}
$$

These integrands are evaluated numerically for $R=2.0a_0$

[18] See for example, Jahnke and Emde, *Tables of Functions*, second edition (Teubner 1933), p. 78.

at over a hundred points and the integrations are performed graphically with the aid of a planimeter. When $\lambda_2=3$, $\mu_2=1.0$ (i.e. $r_{c2}=0$) the integrands become infinite and it is necessary to carry out the integrations analytically in this region. The accuracy of the numerical integrations is considerably decreased by a partial cancellation of positive and negative contributions to the integrals. However, we believe that we have obtained sufficient accuracy for the purposes of this paper. The following is a summary of the numerical values of the second derivatives of the integrals which we used:

(Numbers in units of e^2/a_0 for $R=2.0a_0$)

$L''(aa, bc)=0.029921$, $L''(bb, ac)=0.052345$,
$L''(ab, ac)=0.033504$, $L''(ab, bc)=0.000248$,
$L''(ac, ac)=0.021646$, $L''(aa, cc)=0.058286$,
$L''(aa, ac)=0.059021$, $K''(a, bc)=0.035949$,
$K''(b, ac)=0.058053$, $J''(R_{ac})=0.073263$,
$G''(R_{ac})=0.061640$, $I''(R_{ac})=0.122104$.

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A Mechanical Analyzer for the Solution of Secular Equations and the Calculation of Molecular Vibration Frequencies

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A set of coupled harmonic oscillators has been constructed, so designed that it can be used to solve the numerical secular equations occurring in the theory of the vibration of polyatomic molecules and in other problems. Each oscillator consists of a shaft with cross arms carrying weights to increase the moment of inertia and springs to provide restoring force. The unit is free to rotate about the axis of the shaft, except for the restoring force of the springs. The various units are connected to one another by additional springs. In operation the springs and weights are adjusted to values which represent the coefficients of the secular equation to be solved, the whole device is driven by an eccentric of variable speed, and the frequencies of resonance, representing the roots of the equation, are measured.

KETTERING, Shutes and Andrews[1] introduced the method of analyzing the vibrational spectra of polyatomic molecules by the use of vibrating models consisting of steel balls representing the atoms, connected by springs representing the valence bonds. By vibrating such a model with a motor and eccentric system, the frequencies of resonance of the model can be picked up and measured. Despite the many advantages which this method possesses, it also has certain limitations. It is difficult, for example, to construct a model sufficiently close to the ideal of point masses and weightless springs, especially since the springs must be rigidly attached to the balls and must be capable of resisting tension, compression, bending, and in some cases torsion. For each of these multiple duties the spring must have the proper force constant. The most serious limitation, however, is the lack of flexibility of the apparatus. A model must be built, not only for each molecule, but also for each set of trial values of the various force constants, since the springs are not adjustable. Furthermore, there are many types of potential function which cannot be reproduced by such a model because of geometrical limitations—springs may get in one another's way, for example.

Because of the great power of the Andrews' method, it seemed important to devise a mechanical analyzer that would preserve the advantages and overcome the difficulties mentioned above. In order to achieve this end, the geometrical analogy between the molecule and the model was discarded, since what is really desired is a mechanical system having the same potential and kinetic energies (except for a scale factor) as the molecule. A set of coupled harmonic oscillators forms such a system if the coupling is of the proper form.

[1] Kettering, Shutes and Andrews, Phys. Rev. **36**, 531 (1930); F. Trenkler, Physik. Zeits. **36**, 162 (1935), etc.

Description of Apparatus

The apparatus finally built consists of units, each unit being essentially a harmonic oscillator. A unit consists of a horizontal shaft mounted so that it can rotate in two ball bearings. Perpendicular to this shaft are a number of Duralumin rods which pass through holes in the shaft provided with set screws to hold the rods in place. These rods are parallel to one another and each is grooved from end to end. One of them carries a brass weight on either side of the shaft. These weights give the oscillator unit a moment of inertia which is readily adjustable since the weights may be slid in and out along the rods and held at any point by a set screw. There are also several sizes of weights. See Fig. 1.

Another cross rod, at the end, is used to provide an adjustable restoring force for the unit, this being accomplished by connecting to it two springs the other ends of which are attached to fixed points, one on each side. See Fig. 2.

Such a unit behaves like a harmonic oscillator if the shaft is rotated slightly from the equilibrium position determined by the springs at the end. Gravity has no effect since the two weights are balanced. The frequency of vibration will depend on the position and size of the weights (the moment of inertia of the system about the shaft) and on the restoring force of the springs, which is adjusted by changing the position of the springs on the cross rod.

The complete machine consists of a number of such units (we have actually used five) mounted with their shafts parallel to one another and connected by coupling springs. See Fig. 3. These coupling springs connect one unit with another as desired, using the extra cross rods as shown in Fig. 4. Each unit may be connected with any other (or several other) units, with either positive or negative coupling coefficients. The springs are attached to the rods by means of small connectors which slide on the rods and are held at any point by set screws. These make the effective restoring forces adjustable; they also hold the springs slightly to one side so that crossed springs (Fig. 4a) do not touch each other.

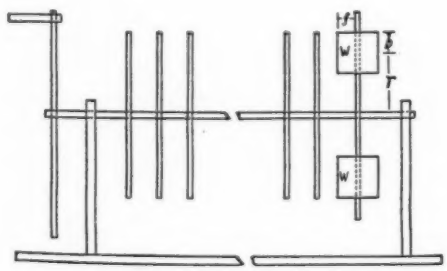

Fig. 1. Side view of one oscillator unit without springs.

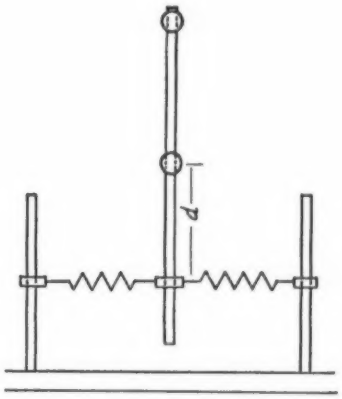

Fig. 2. End view of one oscillator unit showing "positive" springs.

Finally, springs may be connected from the projecting top piece of an end rod to the base below the end of the shaft. Such a spring, called a "negative" spring, (Fig. 5) tends to unstabilize the usual equilibrium position, in contrast to the effect of the "positive" springs illustrated in Fig. 2. They are only used when the coupling springs provide more restoring force to the single unit than is desired. The springs have been wound on a lathe from steel piano wire, most of them from wire 0.037″ in diameter.

The whole mechanism is driven by a light spring which connects one of the cross rods with an eccentric driven through a variable speed reducer with a friction drive, connected to an electric motor. The method of operation, after the constants have been set, is to vary the speed of the driving mechanism until a speed is reached which produces a maximum oscillation of the units. This is a resonance frequency of the machine and at that frequency the units undergo a normal oscillation. The frequency is measured with a stopwatch and a revolution counter on the eccentric shaft.

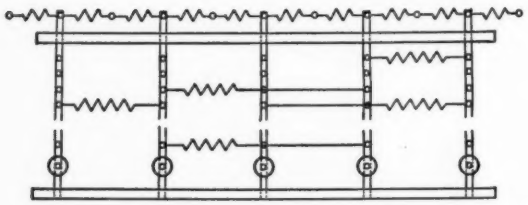

FIG. 3. Top view of five unit machine with arbitrary spring connections.

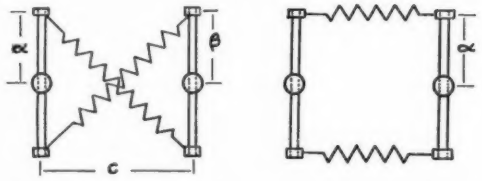

FIG. 4. View along two shafts showing coupling springs. (a) Coupling coefficient positive. (b) Coupling coefficient negative.

PRINCIPLE

The kinetic energy of a system such as the one described above is

$$2T=\sum_{i=1}^{N} I_i\dot{\theta}_i^2, \tag{1}$$

where I_i is the moment of inertia of the ith unit, θ_i is the angular displacement of the ith unit from its equilibrium position, and N is the number of units. The potential energy is given by

$$2V=\sum_{i,\ j=1}^{N} a_{ij}\theta_i\theta_j, \tag{2}$$

in which the constants a_{ij} are determined by the springs. Thus, for $i\neq j$, the magnitude of a_{ij} is determined by the stiffness and position of the springs connecting the units i and j, while the sign of a_{ij} is determined by the mode of connection of these springs (Fig. 4(a) or (b)). The magnitude of a_{ii} is determined by the totality of restoring force due to all the springs attached to unit i, including those connecting it to other units. If the contribution of the coupling springs (a_{ij}) is too small, enough restoring force may be introduced by the use of "positive" springs (Fig. 2) to bring a_{ii} up to the desired values; if the coupling springs contribute too much to a_{ii}, enough may be subtracted by the use of "negative" springs (Fig. 5) to lower a_{ii} to the desired value.

The resonance frequencies of a system with these expressions for the kinetic and potential energies is obtained[2] by the solution of the secular equation:

$$\begin{vmatrix} a_{11}-I_1\lambda & a_{12} & a_{13} & \cdots & a_{1N} \\ a_{21} & a_{22}-I_2\lambda & a_{23} & \cdots & a_{2N} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ a_{N1} & a_{N2} & a_{N3} & \cdots & a_{NN}-I_N\lambda \end{vmatrix}=0, \tag{3}$$

in which $\lambda=4\pi^2\nu^2$, ν being a resonance frequency. Consequently, since the machine may be set with any desired values of the coefficients a_{ij} and I_i, it is evident that a measurement of the resonance frequencies is in effect a mechanical solution of Eq. (3).

APPLICATION TO MOLECULAR VIBRATIONS

In treating the vibrations of molecules, the secular Eq. (3) is obtained as part of the procedure for calculating the normal frequencies and modes of vibration. The quantities a_{ij} have the same significance as before; namely, they are the coefficients of the quadratic terms in $2V$. The quantities I_i are the coefficients in the kinetic energy expression $2T$ but they are not, in the case of molecules, moments of inertia. Their exact molecular significance depends upon the coordinates used to express $2T$ and $2V$.

The simplest coordinate system is one consisting of the Cartesian coordinates of each atom, measured from the equilibrium positions of each atom. In this system the quantities I_i are simply the masses of the atoms. The angles θ_1, θ_2, etc. of the model are to be correlated with the coordinates x_1, y_1, z_1, x_2, y_2, z_2, etc. It should be emphasized that each unit on the machine (and therefore each θ_i) is to be correlated with one coordinate of the molecule and not with one atom. Cartesian coordinates possess the advantage of giving the kinetic energy a simple form. It is usually fairly easy, also, to express the potential energy in terms of such coordinates. The disadvantage of Cartesian coordinates is that the secular equation in terms of them has $3n$

[2] This follows from the standard theory of small vibrations. See Jeans, *Theoretical Mechanics* (Ginn and Co., 1907), p. 348.

rows and columns (n being the number of atoms) and consequently $3n$ units are needed. Six of the roots (for nonlinear molecules) will be zero because of the six motions of translation and rotation.

If $3n-6$ internal coordinates, such as interatomic distances and angles, are used, the rows of the secular equation and the units of the machine are reduced in number to $3n-6$, but it is usually much harder to obtain the expression for the kinetic energy. Frequently such coordinates give the potential energy a very simple form. However, only such coordinates can be used on this machine which throw the kinetic energy into a form without cross terms $\dot{\theta}_i\dot{\theta}_j$.

If the molecule has any symmetry, this may be used to factor the secular equation and then each factor may be solved separately on the machine. There are two ways of doing this in general. One method uses $3n$ coordinates of some sort which are so chosen that they have the same symmetry as the normal coordinates and at the same time give the kinetic energy the necessary diagonal form (Eq. (1)). These coordinates are usually very convenient to obtain and use. However, distributed among the various factors of the secular equation, there will be six roots of value zero, so that some at least of these factors will be of higher degree than is necessary.

In order to eliminate these zero roots one may use $3n-6$ internal coordinates of some sort, having the symmetry properties of the normal coordinates and the property of transforming the kinetic energy into the proper diagonal form. So-called *symmetry coordinates*[3] are such a set of coordinates and are useful if factors up to the maximum capacity of the machine are to be solved. If the factors to be solved are of lower degree than the number of units, it is usually simpler to use the other choice of coordinates ($3n$ in number). Whenever the symmetry is used to factor the equation, group theory is of great utility, especially for more complicated molecules involving degeneracy.

Operation

In order to solve any particular example of Eq. (3) by means of the machine, the springs and weights are adjusted to give the proper values of a_{ij} and I_i, according to the following procedure:

If a pair of springs is connected between the ith and jth units as in Fig. 4(b), the contribution to $2V$ is $2K\alpha^2(\theta_i-\theta_j)^2$, or $a_{ij}=a_{ji}=-2K\alpha^2$, where K is the Hooke's law constant of the springs in dynes/cm and α is the length of the lever arm as shown in Fig. 4(b). There is also a contribution of $2K\alpha^2$ to a_{ii} and a_{jj}.

If a pair of springs is connected as shown in Fig. 4(a),

$$a_{ij}=a_{ji}=2K\alpha\beta\left(1-\frac{l}{g}+\frac{c^2l}{g^3}\right),$$

where α, β, and c are as shown in the figure, $g=(c^2+(\alpha+\beta)^2)^{\frac{1}{2}}$ and l is the length of the unstretched spring. There is a contribution

$$-2K\left[\alpha\beta-\alpha\beta\frac{l}{g}-\frac{\alpha^2c^2l}{g^3}\right] \text{ to } a_{ii}$$

and a contribution

$$-2K\left[\alpha\beta-\frac{\alpha\beta l}{g}-\frac{\beta^2c^2l}{g^3}\right] \text{ to } a_{jj}.$$

If a pair of "positive" springs are connected between the ith unit and fixed rods as shown in Fig. 2, they contribute an amount $+Kd^2$ to a_{ii}.

When it is necessary to reduce the restoring force on the ith unit, a "negative" spring is connected as shown in Fig. 5. This *subtracts* an amount $(Kst\delta)/u$ from a_{ii}, where s and t are as shown in the figure, $u=s+t$, and δ is the

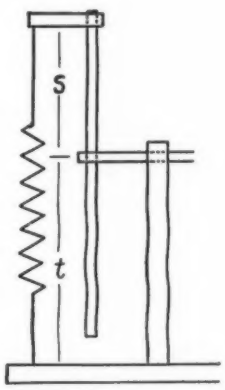

FIG. 5. Side view of end of one unit, showing "negative" spring in place.

[3] J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934).

amount which the spring has been extended from its unstretched length.

The force constants of the springs were determined with an accuracy of 0.2 to 0.3 of 1 percent by hanging a weight of suitable size on the end of the spring and measuring the frequency of oscillation of the pendant weight, from which $K=4\pi^2\nu^2(M+\frac{1}{3}m)$, if ν is the frequency of oscillation, M the mass of the weight hung on the spring and m the mass of the spring. Most of the springs used had a force constant of about 10^5 dynes/cm. Since a_{ij} varies as the square of the distance of the point of attachment of the spring from the axis, it is obvious that a wide range of values can be obtained with a single set of springs.

The moments of inertia of the various units are adjusted to the proper value by fixing the weights (w in Fig. 1) at the proper positions, taking into account the moment of inertia of the shaft, spring arms, etc. The weights make a contribution: $I=2M(r^2+b^2/3+f^2/4)$. M is the mass of one of the pair of weights; r, b, and f are as shown in Fig. 1. The weights used range from 200 grams to 1000 grams.

Since it is impossible to adjust springs and weights so as to obtain molecular magnitudes, some convenient scale factor is introduced. Hence the resonance frequencies of the machine bear a known relation to the frequencies of the equivalent molecule.

It is impossible to make the spring arms absolutely inflexible. The flexibility of the spring arms corresponds to a slight weakening in the springs, increasing as the distance from the axis increases according to the equation: $K_{\text{effective}}=K(1-\gamma\alpha^2)$. γ is determined by measuring the flexure of the spring arm for a known force. This correction is small, amounting only to 3–4 percent at the ends of the spring arms.

As the "negative" springs are somewhat cumbersome to adjust, it is fortunate that in many cases it is possible to eliminate them altogether. If we make the substitution $\lambda'=\lambda+\lambda_0$ in Eq. (3), we obtain a new determinantal equation, the solutions of which are each greater by λ_0 than the corresponding ones of the original equation. In addition, we note that each a_{ii} has been increased by an amount $I_i\lambda_0$. In principle then, we can always eliminate the necessity for "negative" springs by making λ_0 sufficiently large. If the secular equation being solved has one or more zero roots (translation or rotation), the machine will also display modes of motion of zero frequency with the result that it has no stable equilibrium position. This difficulty may be overcome by the use of the substitution just described, which increases all the frequencies. It might also be mentioned here that the usual transformations which leave the value of a determinant unchanged or multiply it by a number, such as multiplying a given row and a given column by a number or adding rows and columns, may often be applied to Eq. (3) to give a determinant which is more convenient to set up on the machine.

The normal frequencies of this machine range from one to ten cycles per second, so that it is a simple matter to observe the amplitudes and phase relationships of the motions of the various units when the machine is in resonance, and thus to obtain the normal mode of vibration corresponding to each frequency.

Accuracy

The five unit instrument at present in use has been tested in a number of ways. The quantitative results, except in especially unfavorable circumstances, have been within about one percent of the calculated values. One series of tests was made in which the symmetrical motions of formaldehyde were studied and these showed that even in such simple applications the labor of using the mechanical method was less than that required to solve the problem analytically.

Phosphorus at High Temperatures and Pressures

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(Received September 20, 1937)

A detailed study of the transformations of the element phosphorus has been carried out at high hydrostatic pressures and at elevated temperatures. This has resulted in the discovery of a new modification of phosphorus, which is noncrystalline in structure and black in color. Its properties have been investigated to a certain extent. Some new calorimetric data are described which shed light on the question of the relative thermodynamic stabilities of this and the other forms of phosphorus.

INTRODUCTION

BLACK phosphorus is formed from white phosphorus by an *irreversible* transition at a pressure of approximately 12,000 atmospheres, and at a temperature of about 200°C. The manner in which this transition progresses with time is most unusual, and it has been studied somewhat in detail by Bridgman.[1] [2] He found the rate of transformation to be not at all regular; it possessed neither uniform acceleration nor exponential characteristics. On the contrary, the process starts out quite slowly, and acceleration is almost imperceptible for about ten or fifteen minutes. At this time there is extremely rapid acceleration, and the transition from white to black phosphorus goes to completion with almost explosive characteristics. During this last part of the reaction more than 90 percent of the total volume change takes place. This fact could be taken as evidence supporting the interpretation of the first slow stage of the reaction as one in which nuclei of the new crystal type are being formed preparatory for the final rapid crystal growth. If this were the case, white phosphorus intermixed with finely powdered black phosphorus would probably transform completely into black phosphorus without the usual preliminary period. However, experiments by Bridgman[3] along these lines have shown this not to be the case. Hence, doubt was cast upon the "nuclei formation" hypothesis, and the whole problem invited further consideration.

New experiments by this author soon pointed to the possible existence of an entirely different type of "black phosphorus" which was responsible for the aforementioned "slow stage" of the transformation. Identification of the new form was carried out first by picnometric and x-ray diffraction methods, and later by measurements of its heat of reaction with bromine. This heat of reaction was sufficiently different from that of the usual type of black phosphorus to establish definitely the identity of a new form.

The question of the relative stabilities of these two forms then naturally arose, and along with it the still unsettled question as to the relative stabilities of red and black phosphorus. Further calorimetric experiments were carried out for information which might settle these points. This data supplemented by other known data on vapor pressure and specific heats served to confirm Bridgman's original hypothesis that black phosphorus was the most stable form of phosphorus at room temperature and atmospheric pressure. And in turn, the new type of black phosphorus from all lines of available evidence appears *less* stable than the original type of black phosphorus.

EVIDENCE FOR A NEW FORM OF BLACK PHOSPHORUS

First of all, a series of experiments at high pressures was undertaken in an effort to gain some information concerning the nature of the process which is responsible for the almost stationary period of about twelve minutes which invariably had preceded the final rapid change into black phosphorus. It is emphasized that during this part of the transformation there is a

* This work done while author was a National Research Fellow.

[1] P. W. Bridgman, J. Am. Chem. Soc. **36**, 1344 (1914).
[2] P. W. Bridgman, J. Am. Chem. Soc. **38**, 609 (1916).
[3] P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, Ltd., London, 1931), p. 384.

small but unmistakable change in volume. This itself could be used roughly as an indicator of the progress of the reaction, and an attempt could be made to interrupt the same at any desired time before its completion.

The white phosphorus was placed under pressure in a small cylinder provided with a heating coil and thermocouple. To avoid contact between the active white phosphorus and the steel cylinder wall, the former was enclosed in a thin lead capsule. *After* the pressure was adjusted to a desired value, the temperature was raised. The reaction would now begin, and when it had progressed any desired amount, the pressure was suddenly reduced to about half its highest value, in an effort to check further progress. A complete reduction in pressure was avoided since it would allow any untransformed white phosphorus to pass over into a liquid phase, whence, at the existing temperature, it would immediately be changed into red phosphorus. The reduction to half-pressure would, at least, suffice to keep the phosphorus always in the solid state, and hence eliminate this hazard. And it was reasonable to expect that a partial reduction in pressure of this nature would be sufficient to stop further progress of the transition immediately. The temperature could then be reduced to that of the room, the remaining pressure released, and the sample removed for inspection.

Six runs of this type were made. The pressure in each was about 13,000 atmospheres, and the temperature approximately 205°C. The samples were identical as to source of material, size, shape, etc. The only difference in the individual procedures was in the elapsed times allowed from the attainment of reaction conditions to the first reduction in pressure. This time was varied for the individual samples in steps of about two minutes each, so as to space them evenly over the fifteen minute period. After cooling, the samples were removed from the press and washed with CS_2, which served to dissolve out any untransformed white phosphorus. Upon examination each sample was found to contain a carbon-like powder residue. The amount of this bore a direct correlation to the length of time the reaction had been allowed to progress. A visual inspection suggested that this residue was not the usual crystalline black phosphorus, which is quite similar to graphite in appearance, whereas this substance was definitely more "sooty" or carbon-like. A density determination (flotation method) gave the value 2.25 which is quite far from that of Bridgman's black phosphorus which has a density of 2.69.

As a further test for the identity of this lower density black phosphorus, x-ray diffraction pictures were used. A number of these were taken employing the usual Debye-Scherrer type of powder camera and a copper target x-ray tube. Under these conditions, Bridgman's black phosphorus gives sharp lines belonging to an orthorhombic type of crystal structure.[4] However, under no circumstance whatsoever, would the new black phosphorus give diffraction lines. This would clearly indicate that either the new form is an amorphous material, or that it is microcrystalline in structure.

In case the latter proved to be the correct interpretation, it would still be impossible to say whether or not the microcrystals were, except for size, identical with Bridgman's black phosphorus. If they were, there should be only at most a very small difference in the heat content of the two forms. Values for the difference in the thermodynamic total heats could be obtained by means of a calorimetric measurement of the heats of reaction of these forms of phosphorus in some reaction which would lead to the same end product for each. Measurements of this nature were taken and are completely described in a later part of this paper. What is important at this point is the fact *that a difference of over 14 kilojoules per gram-atom was found between the heat contents of the two forms*. The experimental error could not account for more than 5 percent of this difference.

These measurements, then, seem to give conclusive evidence for a new form of black phosphorus, which is noncrystalline, at least as far as x-ray patterns go, and which is *definitely not* the same *polymorphic form* ordinarily called *black phosphorus*.

Time–Pressure–Temperature Relations

The existence of this new form of phosphorus complicated the problem as a whole. Accordingly,

[4] R. Hultgren, N. S. Gingrich, B. E. Warren, J. Chem. Phys. **3**, 992 (1935).

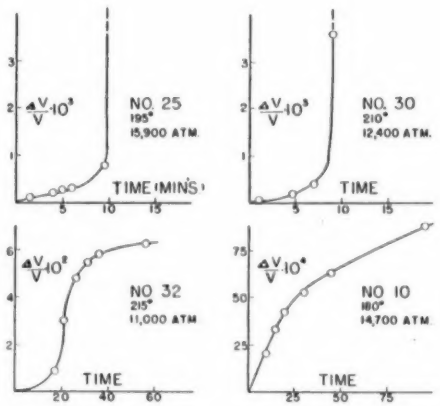

FIG. 1. Progress of transitions. These curves show the extent of the transition ($\Delta v/v$) *versus* time. The upper curves are typical for transitions leading to black crystalline phosphorus, the lower for transitions leading to noncrystalline black.

some new experiments were tried in an effort to isolate transitions which would involve only one type of black phosphorus. The method used was perfectly straightforward. White phosphorus was subjected to a wide variation of temperatures and pressures in a rather extended series of experiments. In each case the progress of the reaction was plotted against time: i.e., in Fig. 1, $\Delta v/v$ *vs.* time. As a further check on what the transition actually involved, the phosphorus was examined in each case for structure and density, immediately after removal from the apparatus. A direct correlation between these properties and the rate of reaction curve was soon made evident. It will be noticed that in this same figure the upper curves are pretty much alike in having a steep vertical section which indicates a final rapid conclusion to the transition. The lower curves are different; they slope off toward the horizontal after a considerable lapse of time, indicating a slow exponential termination of the reaction.

The correlation referred to then is that the lower type of curve leads invariably to the formation of black noncrystalline phosphorus alone. On the other hand, the upper type of curve consistently leads to the crystalline form. Hence it could be said that a complete isolation of the reaction of the white phosphorus to noncrystalline black is possible if temperature and pressure are correct. Whether or not the transition could be made to go from white phosphorus *directly* into crystalline black was still uncertain, since there was no way of knowing if the formation of noncrystalline black was a necessary part of this reaction. Aside from this point there was still the question of a new P-T diagram which would include noncrystalline phosphorus. Accordingly, the P-T region was systematically covered by a series of some forty odd experiments. These were designed to give pertinent information both for a revised diagram and for settling the question of a possible complete isolation of the black crystalline reaction.

In this series of runs, certain pressures were chosen (from 11,000 to 16,000 atmos.), and the effect of a variation in temperature at each was noted. In order to get accurate timing of the transition speed, the experimental procedure was somewhat modified from that previously described. The difficulty, of course, had been that the temperature rise is, of necessity, slow, and consequently the transition will start *before* the maximum temperature for that run is attained. To raise the temperature first and then apply pressure is completely disasterous, since this procedure will first melt the white phosphorus and consequently will allow it to pass over into red phosphorus. To circumvent both of these failings, a pressure of about 7000 atmos. was first applied, and then the temperature was raised to its final value. Under these conditions the phosphorus remains in the solid state as white phosphorus. Any time after this, the final pressure may be quickly applied (in a few seconds time), and the progress of the transition observed from that point on. Using this procedure one has an accurate knowledge of what happens from the instant that experimental conditions are attained, and the issue is not confused by the transition starting at some unknown time.

In Fig. 2 the results of some representative experiments are plotted. These curves show the time for the "complete" reaction plotted against temperature. It is emphasized that *time* here is recorded from the instant attainment of final pressure to the observation of the "collapse in volume" which is indicative of the completion of the transition into black crystalline phosphorus. Most noteworthy of the features of these curves is that apparently for every pressure at which the transition can be made to take place it *can be made to do so instantaneously* providing the

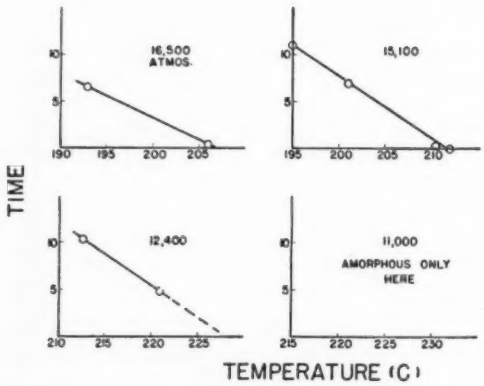

FIG. 2. Reaction times. Time for transitions to black crystalline phosphorus against temperature for several different pressures. At sufficiently high temperatures, the curves always cross the origin of the time axis.

temperature is sufficiently high. A second important feature is that in these experiments it was found that, if there was no collapse in volume in a time of about ten or fifteen minutes, the transition would not result in the formation of black crystalline phosphorus at all, but would continue as a simple reaction into black noncrystalline phosphorus.

On the basis of these observations the data could be plotted on a P-T diagram as has been done in Fig. 3. Here three regions are apparent. Points lying in region (3) indicate that at the corresponding temperature and pressure, there is an instantaneous reaction. In region (2) the transition is accompanied by a preliminary period. While, finally, in region (1), only the transition to black noncrystalline phosphorus is possible.

The existence of this "instantaneous" reaction is new. The fact that it does exist clears up to a certain extent the mystery which previously had been ascribed to the "delayed" transition. However, it would still be impossible to say that the transition to black crystalline phosphorus had not been accompanied by a partial transition to black noncrystalline just as in the former cases. The higher temperature could account for a general acceleration of both reactions so as to make them indistinguishable. Just what part the transition to noncrystalline black played in cases coming in region (2) likewise was not clear. Two suggestions are almost self-evident. The first is that the transition goes from white phosphorus to black noncrystalline to black crystalline. The second is that the heat of formation given off when black noncrystalline phosphorus is formed at a temperature and pressure at which *it alone* could be formed, is sufficient to heat up the remaining untransformed white phosphorus to a temperature sufficiently high to enable it to transform into the black crystalline form.

The first suggestion was tested quite simply by preparing a sample of pure black noncrystalline phosphorus, and subjecting it to an elevated temperature and pressure to see if it would transform into the black crystalline form. In this experiment, it was taken to a pressure of 15,000 atmospheres and to a temperature of 300°C *without* a change of form. This, then, definitely ruled out the suggestion of a two-step reaction: phosphorus does *not* go from white to black noncrystalline, to black crystalline. The question now asked was this: Would the amount of heat generated by a fractional part of the phosphorus going over into the noncrystalline black form be sufficient to raise the temperature of the entire mass any appreciable degree? This could be answered decidedly in the affirmative, with the aid of the heat content differences given in the next section of this paper. For instance, a *one-percent* conversion into the noncrystalline form would account for a temperature rise of 26° throughout the entire mass, if the conditions were adiabatic.

As a further test along these lines experiments were tried under a number of different conditions in regard to thermal isolation of the phosphorus sample. For this purpose a number of odd shaped lead containers were prepared for the phosphorus.

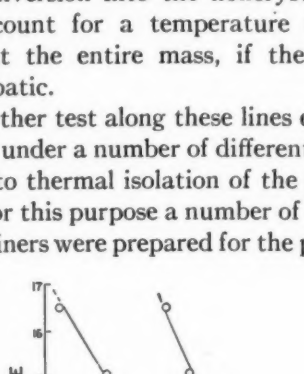

FIG. 3. P-T diagram of phosphorus. Region (3) indicates an "instantaneous" transition to black crystalline phosphorus, region (2) a delayed transition, and region (1) transitions only to noncrystalline phosphorus.

These are shown in Fig. 4. The normal type of container is the simple lead cylinder closed at both ends which is shown mounted in place in the high pressure steel cylinder in the upper part of Fig. 4. The blackened portions in all cases represent the lead, the dotted portions the phosphorus. Container (6) was designed to give the highest degree of thermal isolation since it is lined with soapstone. The general conclusion arrived at from the use of these containers was that the heat conductivity from the phosphorus to the steel wall played a very important part in the transitions. For instance, using containers of the type (1), one would have a condition in which all of the phosphorus was near the metallic outer wall, and hence the thermal isolation would be very poor. And, indeed, it was found with this type of container that at 14,000 atmospheres the transition temperature was 10° higher than with the ordinary simple container. The explanation would apparently be that all of the phosphorus is quite near the outer wall and consequently cannot easily acquire a temperature much higher than it. Consequently heat developed by a partial transition to black noncrystalline phosphorus does not serve to heat the phosphorus to a considerable extent but simply passes off into the steel cylinder. An opposite but smaller effect was found with container number (6), which afforded the highest degree of thermal isolation. It was further revealed in its use that it produced the most perfect specimen of black phosphorus that the author has ever seen. The crystals were large and grew out to the very edge of the container. Usually the phosphorus is pure only in the center of the specimen, and as one examines the edges he finds increasing amounts of the different polymorphic forms (red, etc.) there.

Containers (4) and (5) provided a thermal gradient along the axis of the sample due to the conical shaped lead center part. They produced nothing new or startling, but simply gave in an axial direction the kind of results which had previously been observed when the gradient was all radial. Several containers of the type (3) were used to see if growth from a central nucleus could be observed. By this one means growth of crystals in a manner whereby a crystal starts somewhere and grows rapidly at the expense of the material in the surrounding regions. The idea

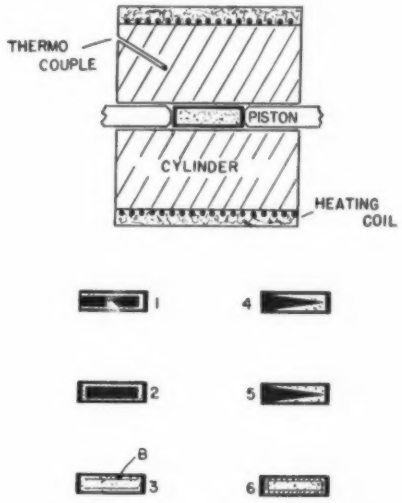

FIG. 4. Types of lead containers. The upper diagram shows the pressure cylinder with a simple type of lead container for the phosphorus. The lower diagrams show various types of containers used to give different degrees of thermal isolation of the phosphorus.

of container (3) then was to impair this type of growth by the imposition of the artifical metallic barrier (B). At the same time the barrier would be sufficiently light so as not to materially effect the thermal conditions within the lead capsule. In no case of this kind was there any observable effect due to this type of barrier. Likewise, all attempts to ascertain a preferred orientation of crystals in these experiments were without success. Hence, it was concluded that the crystalline growth was not much dependent upon "seed crystals," but that the important factor in the whole question was temperature.

The general conclusions of this section are that there is *no* transition from black noncrystalline phosphorus in the ordinary experiment.[5] The part that black noncrystalline *does* play is to furnish heat when it is formed in quantities sufficient to raise the temperature of all of the phosphorus sufficiently high to enable a transition to black crystalline phosphorus to take place. As a result of this connection between the two forms of black phosphorus it is impossible to give accurately the regions in a P-T plot in which

[5] It has already been mentioned that this transition will not occur at 14,000 atmospheres and 300°C which is undoubtedly a higher temperature than is usually reached during a transition with the outer cylinder at 200°C. In another experiment, employing an internal furnace this transition was made to run at 12,000 atmospheres at temperature of 500°±50°.

the one or the other is formed. There will always be a region like region (2) in Fig. 3. And, finally, the degree of thermal isolation is important in the experiment since the transition temperature is a function of it.

Relations of the Various Polymorphic Forms

This section is concerned with the measurement of the differences in the total heats between the various forms of phosphorus. They were obtained from the heats of reaction of the different kinds of phosphorus with bromine. The purpose of such measurements was twofold. In the first place, the large difference in heat content between the two forms of black phosphorus has already been mentioned as serving as partial evidence favoring the identity of black noncrystalline as a separate polymorphic form. The second purpose of the measurements was for a further attack on the now time-honored problem[6–11] of the relative stabilities of black and red phosphorus. A description of the experimental procedure follows:

A special balanced null method calorimeter was built for the measurement of the heats of reaction for the different samples of phosphorus. It was composed of two identical calorimeters immersed in the same constant temperature bath (constancy of 0.01°). The heat capacities were adjustable by simple addition or removal of water. For these experiments they were made equal to about 1 kg water equivalent. A ten junction copper-constantan thermopile of about 15 ohms resistance ran between the two calorimeters, giving a sensitivity with the galvanometer used of 3900 millimeters per degree. With this sensitivity and heat capacity the calorimeter was accurate to about one-tenth of a calorie in one hundred calories, and its constancy with time sufficiently reliable so as not to impair the above figure for accuracy if the heat was added over a period of as long as two hours. The method of using the dual instrument was to always keep the two calorimeter temperatures quite the same by passing an accurately measurable current through a heating coil in the colder of the two until the desired temperature balance was attained. Since the relative heat capacities of the two calorimeters were accurately known, the heat formed by a given reaction could be measured by the current used to balance it in the other. The reaction proper took place in a small glass bulb immersed in the constantly stirred water within the calorimeter, the glass bulb being connected to the exterior by means of small bore tube sealed to it. The procedure was then as follows: The calorimeters were brought to a constant and equal temperature. A weighed amount of phosphorus was then dropped into the glass bulb of one. The bromine solution had previously been poured in. Heating by means of a current was then started in the other and the temperatures maintained equal until the reaction had run to its final completion (about two hours). Due to the long time involved for the reaction, it was fortunate that the balanced type of calorimeter was used. A second experiment was always run in which the reaction took place in the other calorimeter.

The preparation of the phosphorus for the experiment was as follows: The various samples were powdered and screened through a 100 mesh screen, washed out with CS_2, dried, shaken with $CaCO_3$ and water, rinsed in water, washed in dilute HNO_3, again rinsed, and finally dried for several hours at 75°C. It was then accurately weighed out into samples of nearly 100 mg each. A 30 cc volume of the bromine mixture (6 parts CS_2 to one part Br_2) was used to provide an ample excess of bromine to insure a complete reaction. Now, there is a heat of solution of PBr_5 in C_2S and Br_2 varying with the concentrations involved. Hence, in each experiment the same amount of phosphorus was used and likewise the same amount of the bromine solution which was mixed in a large quantity to supply the whole series of experiments. In this manner it was ensured that the heat arising from such a source would in all cases be the same, and for the purpose in hand could accurately be canceled out.

The results of the calorimetric determinations are given in Table I; the heats of reaction here

[6] A. Smits and S. C. Bokhorst, Proc. Amst. Acad. **17**, 962 (1915).
[7] A. Smits, G. Meyer and R. Ph. Beck, Proc. Amst. Acad. **18**, 992 (1915).
[8] A. Smits and S. C. Bokhorst, Zeits. f. physik. Chemie **91**, 3, 249 (1916).
[9] A. Smits, Comptes rendus **26**, Nov. (1928).
[10] A. Smits, Comptes rendus **28**, Jan. (1929).
[11] See reference 1.

given include all heats of solution, etc. which add to the total heat under the experimental conditions as outlined above. By subtracting the heat of solution of any one type of phosphorus from that of another we obtain the difference in heat content ΔH.

As far as establishing the identity of black noncrystalline phosphorus is concerned these results seem quite conclusive. The difference in heat content between it and black crystalline phosphorus produced from the identical white stock is about 30 kilojoules per gram atom. Since the probable error of an individual measurement is of the order of $\frac{1}{2}$ kilojoule per gram atom, the above figure appears to be quite significant.

The difference of 7.2 kilojoules per gram atom between the recent black crystalline phosphorus and that of Bridgman produced in 1914 should be explained. The magnitude of the difference is certainly too great to be accounted for by experimental uncertainty. It is, however, reasonably accounted for if one assumes that Bridgman's phosphorus was not uniform in a polymorphic sense, i.e., that it contained several polymorphic forms. In this connection it has already been mentioned that a thermal gradient generally exists in a phosphorus sample during the time that it is undergoing its polymorphic transformation. It has likewise been shown that the hotter (inner) portions will favor a transformation to black crystalline phosphorus, whereas the outer, cooler portions will probably go to a large extent into noncrystalline phosphorus. This phenomenon was especially pronounced in the experiments in which the gradients were purposely made large. Now, in selecting the samples for the calorimetric work, there was only a limited supply of the 1914 phosphorus, and consequently it was taken pretty much as it came. (Presumably it was not pure black crystalline.) In the case of the recent phosphorus the supply was large and the selection of the samples could be made with considerable care. This undoubtedly could account for the difference observed in the heat content values. The question might be asked, if the presence of the less dense noncrystalline form might not be detected due to the lowering of the density of the whole mass which it produces. Unfortunately it cannot, where the flotation method of density determination must be used, since it will give the density of the more dense (pure) particles only.

The last problem concerns the relative thermodynamic stabilities of the various forms. First consider the case of red and of black crystalline. Bridgman[15] first worked on this employing the method of specific heats, but finding this not

[12] Ogir, Comptes rendus **92**, 83 (1881).
[13] H. C. Duss, Thesis 1924, Mallinckrodt Laboratory, Harvard University.
[14] P. W. Bridgman, Phys. Rev. **45**, 844 (1934).
[15] See reference 1.

TABLE I. *Heats of reaction of different types of phosphorus with bromine.*

Type of Phosphorus	Heat of Reaction (H)	Average (H)	Difference ΔH
(1) Black Crystalline	152.2 kilojoules / gram-atom	153.2	
(Recent)	154.1 "		
			7.2 kilojoules / gram-atom
(2) Black Crystalline	161.2 "	160.4	
(Bridgman's 1914)	159.7 "		
			16.4 "
(3) Commercial Red	177.2 "	176.8	
	176.5 "		
			1.1 "
(4) Laboratory Red*	177.8 "	177.9	
	178.0 "		
			6.6 "
(5) Black Noncrystalline	184.0 "	184.5	
	185.0 "		
			64.5 "
(6) White	See references 12 and 13.	249.0	

* This phosphorus produced under nitrogen pressure of 6000 atmospheres and at a temperature of 300°C. These conditions maintained for 6 hours.

TABLE II. *Vapor pressures of phosphorus.*

TEMPERATURE	VAPOR PRESSURE (cm of Hg) Black	Red
357.1°C	2.3	5.2
443.7°C	—	73.2
445.2°C	58.5	—

TABLE III. *Vapor pressure of phosphorus.*

TEMPERATURE	VAPOR PRESSURE (in atmospheres) Black	Red
515°C	8.5 (increasing)	10.5
553°	19.3 "	21.5
567°	28.6 (constant)	28.5
578°	39.5 "	35.0

sufficiently sensitive turned to vapor pressures. On the basis of these measurements he found black phosphorus to be the more stable form since its vapor pressure was the lower. Bridgman's results are given in Table II.

These results are very definite in attributing a lower vapor pressure to black phosphorus at both temperatures, and hence in pronouncing it the more stable form of phosphorus.

The results of Smits[16] and his colleagues are given in Table III.

It will be noticed that below 560° *black* phosphorus has a lower vapor pressure, and above that *red* has the lower. Ordinarily we would take this to indicate that black was the stable form below 560° and *red* above. However, Smits regards this as an extremely unlikely situation, and points to an apparent metastability of black phosphorus below 560° as a solution of the problem. Among other evidence in favor of this he gives the experimental observation that he has made to the effect that the vapor pressure below 560° is not constant for black phosphorus but apparently increases with time, this indicating a disturbed condition of "inner equilibrium" in the solid phase of the black phosphorus. As further evidence in favor of this interpretation Smits cites the fact that he has found the triple-point of black phosphorus to be slightly lower than that of red.

Now, since the temperature ranges covered by the observations of Bridgman and Smits do not overlap, there is no actual conflict in the experimental data. However, their conclusions are in direct contradiction.

Since one can obtain from vapor pressure data of this type, a value for the difference in the heat contents between the two forms of phosphorus, it is possible to compare this vapor pressure data with my calorimetric results. The thermodynamic equation,

$$\frac{d(\log p)}{d(1/T)} \cdot R = H_v \text{ (Heat of Vaporization)}$$

gives the heat of vaporization from the vapor pressure curve. Now, if one obtains in this manner the heats of vaporization at a certain temperature for the two kinds of phosphorus under discussion, and subtracts one from another, the result will be equal to the difference in heat contents. These, then, may be compared with the values in Table I.

In Fig. 5 the author has plotted the data of Smits and of Bridgman. The points from the data of the latter are connected by dashed lines. The solid lines attempt to connect points given by both. The failure of the curves to continue as straight lines in the region of 560° is a bit distressing, and may have some significance as Smits has indicated. In the lower temperature regions the curves do approximate straight lines. Only in this region can the slopes of the two lines be determined with any accuracy. The change in slope of the lines in the region of 560° is far too

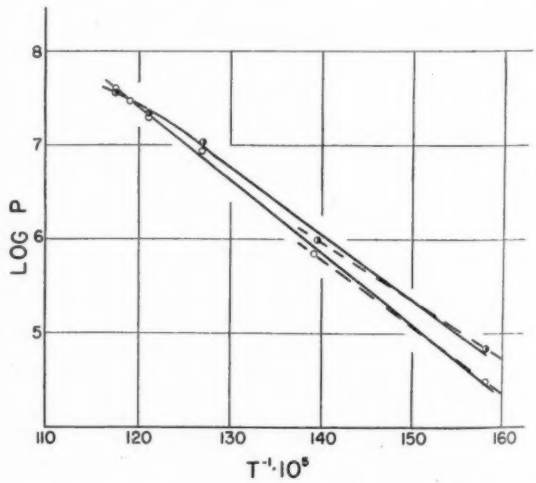

FIG. 5. Vapor-pressure *vs.* 1/temperature. The lower curve is for *black crystalline*, the upper for *red*. Points connected by dashed lines are Bridgman's, the others are Smits'.

[16] See reference 7.

rapid for accurate measurement, and a slight experimental error in a vapor pressure measurement would be greatly magnified in a calculation of a heat of vaporization. Consequently the only check with the calorimetric data[18] which would have any meaning is in the neighborhood of 350°C. Here Bridgman's data give a value of 19.1 kilojoules per gram atom as the difference in total heats between black (1914) and red phosphorus. This compares favorably with the value of 17.5 which one obtains from Table I. Apparently, this agreement would tend to support the validity of the vapor pressure data for black phosphorus below 560°. At the same time, it would cast some doubt on Smits' hypothesis of the metastability of black phosphorus in this region. This follows from the fact that Smits has placed emphasis on the fact that the data for black phosphorus below 560°C is not good since constant values cannot be obtained. The tendency, he says, is always toward an increase, and presumably toward a value *higher* than that of red phosphorus. Were this the case, there would be no agreement with the calorimetric values like that indicated above, since the data for the black phosphorus would admittedly be incorrect.

As a consequence, it seems reasonable to conclude, that black phosphorus below 560°C is the stable form of phosphorus.

Now, glancing again at Table I, one is confronted with a progression of this nature: black, red, white. This is the order of the stabilities, the order of the total heats, and the order of the densities. As far as density and total heats are concerned, black amorphous phosphorus belongs between red phosphorus and white phosphorus. One is tempted to argue by analogy and place black amorphous phosphorus there also in order of stability. Of course, there is no thermodynamical justification for so doing. Quite by accident, however, it was discovered that after prolonged heating at about 125°C black amorphous phosphorus could be transformed into a brilliant violet form of phosphorus, this of course, being a form of red phosphorus. Naturally, now one could positively say that at least at 125°C *red was more stable than black amorphous*, and this would in turn place black crystalline *above* black amorphous in order of stability.

In conclusion, the author gratefully acknowledges the help he has received on this problem from Professor Bridgman.

[18] This comparison of calorimetric data at 20°C with vapor pressure data at 350°C is only justified by the fact that there is no measurable difference in the specific heats of black and of red phosphorus.

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An Electron Diffraction Study of the Grain Boundaries in Iron

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Grain boundary membranes, left after the dissolution of iron in ammonium persulphate solution, were studied by means of electron diffraction to determine whether crystalline materials are present in the membranes, and if present to identify the crystals. Samples of untreated and heat-treated transformer iron, and heat-treated electrodeposited iron were used. It was found that heat-treated electrodeposited iron left residues which were suitable for study by electron diffraction when supported by Resoglaz backing films. From the electron diffraction patterns obtained, identification was made of the presence of Fe_3C and of αFeOOH. It is suggested that the αFeOOH did not exist originally in the grain boundaries, but may have been formed by some chemical reaction either between iron and ammonium persulphate, or between some grain boundary constituent such as an iron oxide and the persulphate solution. The method of studying grain boundary materials does not afford a complete analysis, but it is believed that it makes possible important contributions since the presence of crystalline materials in the residues may be detected.

Introduction

THE material present in the space between grains of a metal is commonly designated as grain boundary material, or grain boundaries. Much has been written about its influence on the physical and chemical properties of metals, and in particular, on its effect on the recrystallization and grain growth of metals. Little work has been done, however, to determine the exact nature of the substance.

Rosenhain[1] regarded the material as an amorphous metal, or cement, holding the grains together with very much the same properties as the Beilby amorphous surface layer on polished metals. This hypothesis has been used to explain the alteration of many of the properties of metals when subjected to mechanical and thermal treatment. Sauveur[2] has given an excellent summary of the theory of Rosenhain as well as elaborations upon it by other authors.

G. Tammann has made the most extensive and direct investigations of grain boundaries. He[3] showed that after dissolving certain metals, the material between the grains is left as a residue. This residue is a membrane which has a sponge-like or honey-combed structure—the empty spaces corresponding to the position of the metal grains which have been dissolved. He found that this membrane is so fine and fragile that when the dissolution of metals in acids is accompanied by evolution of gas, the escaping bubbles tear and completely destroy the membrane. When no gas is evolved, as when a lamina of cadmium is dissolved in ammonium nitrate solution, he found that the remaining residue consisted of a very thin, gray, honey-combed film which retains the shape of the original metal lamina. Tammann believed that this film consisted of oxides which form a skin surrounding the individual metal grains. He made similar observations on zinc, but found that the grain boundaries are invisible unless several drops of water saturated with ammonia were added to the ammonium nitrate solution. The ammonia water serves to dissolve the zinc hydroxide which forms during the dissolution of the metal.

Von Kutzelnigg[4] dissolved pieces of tin foil in a 10 percent iron chloride solution and obtained a small residue in the form of a cohesive, light yellow film, outlining the form of the original foil. He identified the substance as grain boundary material and by a qualitative chemical analysis he deduced that it was a tin compound.

Tammann and his co-workers made further studies of grain boundary residues left after the dissolution of certain metals containing small known quantities of different admixtures. Tammann, Heinzel, and Laass[5] traced with the microscope the distribution of small known admixtures of lead, bismuth, antimony, and tin in the grain boundaries of cadmium. They showed how small quantities up to 0.1 percent of these materials in cadmium can be determined readily by the use of such observations in conjunction with microchemical analysis. They also studied copper and showed how the presence of admixtures of lead, bismuth and antimony can be detected by examining the grain boundary residue. Tammann and Kalge[6] dissolved laminae of electrolytic iron in a solution of ammonium persulphate and by examining the grain boundary residue microscopically were able to detect as little as 0.002 percent ferrous sulphide, less than 0.05 percent aluminum, 0.05 percent antimony, 0.02 percent tin and 0.001 percent silicon. Tammann and Heinzel[7] studied the distribution of admixtures of lead and copper in grain boundary residues of cadmium and thereby determined solubility temperature curves for binary cadmium systems containing lead and copper.

Tammann and Dreyer[8] studied the influence of grain boundaries on the grain size of lead. Thin plates of lead were dissolved in acetic acid-hydrogen peroxide solution. It was concluded that in order to obtain lead of small grain size, about 0.1 percent of copper should be added.

[1] Walter Rosenhain, *Physical Metallurgy* (Constable & Company Ltd., London, 1914), p. 245.
[2] Albert Sauveur, *The Metallography and Heat Treatment of Iron and Steel* (McGraw-Hill, New York, 1935), p. 17.
[3] G. Tammann, Zeits. f. anorg. allgem. Chemie **121**, 275 (1921).
[4] Artur Kutzelnigg, Zeits. f. anorg. allgem. Chemie **202**, 418 (1931).
[5] G. Tammann, A. Heinzel and F. Laass, Zeits. f. anorg. allgem. Chemie **176**, 143 (1928).
[6] G. Tammann and W. Kalge, Zeits. f. anorg. allgem. Chemie **176**, 152 (1928).
[7] G. Tammann and A. Heinzel, Zeits. f. anorg. allgem. Chemie **176**, 147 (1928).
[8] G. Tammann and K. L. Dreyer, Zeits. f. anorg. allgem. Chemie **191**, 65 (1930).

In a paper on recrystallization of metals, Tammann[9] described the changes which take place when metals are cold worked. Each grain is surrounded by a complete skin when it crystallizes out of the melt. He showed that when the metal is cold worked as in rolling, the skin is so torn by the elongation of the grains that after the dissolution of the rolled plate nothing of the original honey-combed structure can be seen in the residue. If the metal is heated subsequently to a sufficiently high temperature, the newly formed grains are surrounded by complete skins and on dissolution the honey-combed structure is again apparent.

The existence of the grain boundary residues in the form of thin films, as described by these workers, suggested an electron diffraction study of the material. Such a study was accordingly undertaken in the case of iron with the hope of determining whether or not crystalline materials are present in the grain boundaries, and if so, to determine what these materials are.

Experimental Procedure

Transformer iron was first chosen because it was believed that the high silicon content would make for strong boundary residues. A series of experiments with the iron, however, indicated that the residues were too thick to obtain satisfactory diffraction patterns. Electrodeposited iron was then used and it was found that when the grain boundary residues were properly supported, satisfactory diffraction pictures could be obtained. It is believed that the experimental work done on the transformer iron is of interest and is accordingly described.

Transformer Iron

The chemical composition of the transformer iron is shown in Table I. Laminae of the metal about $4\times6\times0.2$ mm in size were used. The laminae were carefully cleaned and the surfaces polished on fine emery paper to remove all visible oxide films. Immediately after polishing, the specimens were degreased with carbon tetrachloride, and then placed in small petrie dishes containing a 12 percent solution by weight of ammonium persulphate. These dishes were placed on a large block of ice and allowed to stand until the metal grains were completely dissolved, which required about 16 hours. The low temperature was necessary to prevent rapid evolution of gas.

The first observable reaction of the ammonium persulphate with the laminae was the etching of the surfaces. Then, after several hours, the surfaces usually became black and remained so until all the iron was dissolved, or at least the specimens had become flexible. The black coating now slowly disappeared leaving brown membranes which underwent no further visible changes until they were dried.

After the complete dissolution of the metal grains, the grain boundary residues were washed by a slow stream of distilled water until no acidity could be detected. An excess of alcohol was then added slowly to lower the surface tension as much as possible below that of water. The films could then be mounted readily over the 0.1 mm holes of the specimen holders of the electron diffraction camera.[10] A microscopic examination, however, of the grain boundary specimens while they were still in the water showed that they were nonuniform and torn, brownish in color and possessed large deposits of black material. Since such films are rather unsatisfactory for electron diffraction study, the metallic laminae were treated to see if a recrystallization as described by Tammann[9] would produce a more uniform grain boundary skin.

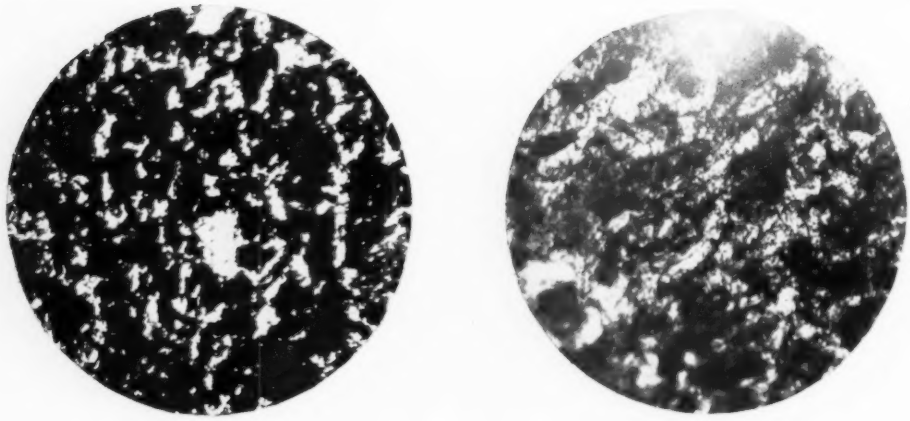
The laminae were pounded on an anvil until they were reduced to roughly half their thickness, and then heated in an oven to a bright red color and allowed to cool slowly. The surfaces of the specimens were then cleaned and polished as

Table I.

	Electrodeposited Iron	Transformer Iron
T. Carbon	0.015%	0.018%
Manganese	None	.078
Phosphorus	None	.008
Sulphur	.005	.030
Silicon	.003	4.373
Slag and Oxide	.700	Trace
Copper	.013	.036
Nitrogen	None	.0014

[9] G. Tammann, Zeits. f. anorg. allgem. Chemie **185**, 41 (1929).

[10] R. Morgan and N. Smith, Rev. Sci. Inst. **6**, 316 (1935).



(a) (b)

FIG. 1. (a) Not heat treated. (b) Heat treated.

before and the specimens were placed in the persulphate solution for dissolution.

A very marked difference was observed between the films prepared from the heat-treated iron and those from the untreated. Figs. 1(a) and 1(b) are microphotographs taken of the films while still in water. Although much of the difference in appearance is lost in the microphotographs, considerable difference can still be seen. A portion of the picture 1(b) shows slight distortion due to the fact that part of the film was not well in focus.

The grain boundary material from the heat-treated iron (Fig. 1(b)) is much more uniform than that from the untreated iron (Fig. 1(a)) and has fewer black inclusions. Moreover, the residue from the heat-treated iron was an untorn network retaining the shape of the original lamina, and was much more transparent than the residue from the untreated iron.

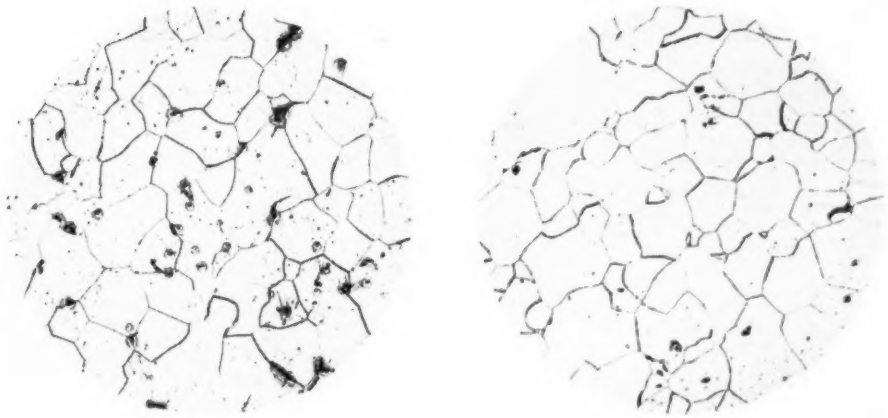
Because of the difference in these two residues, microphotographs were made of etched surfaces of heat-treated and untreated laminae of the iron to compare their grain structures. These photographs are shown in Figs. 2(a) and 2(b). The black inclusions which are rather numerous in the untreated specimens (Fig. 2(a)) are seen to be very much diminished in the heat-treated specimens (Fig. 2(b)).

When the grain boundary specimens from the heat-treated iron were mounted in preparation for making the electron diffraction pictures, it was observed that after drying the films puffed up, became fairly thick, quite brittle and powdery. They also turned gray in color, although by transmitted light they were still reddish brown. In the great majority of cases no diffraction patterns could be obtained; there was only a general blackening of the photographic plate. Now and then a few rings appeared and in a few cases, portions of Laue patterns were obtained. It was believed that the films were too thick to give good patterns and a great many attempts to get thinner films were unsuccessful.

ELECTRODEPOSITED IRON

Electrodeposited iron with the chemical composition shown in Table I was used. This iron was obtained from the National Bureau of Standards.

It was found that the grain boundary residue of electrodeposited iron was a uniform, honeycombed film, brown in color, very much thinner and more fragile than that left in the case of transformer iron. In fact, the slightest disturbance of the solvent so completely destroyed the film that scarcely a trace remained. Accordingly, utmost care had to be used in washing the film and in introducing the alcohol into the petrie dish. Instead of placing the lamina directly in the petrie dish, as was done with transformer iron, it was first placed in a small crystal glass which in turn was placed in the petrie dish. After the lamina was dissolved and the residue washed in the usual way, the water was pipetted out of the petrie dish and alcohol was added to the dish



(a) (b)

FIG. 2. (a) Not heat treated. (b) Heat treated.

until level with the edge of the crystal glass. This set-up was covered with a bell jar and allowed to stand for several hours. During this time enough alcohol vapor passed into the water in the crystal glass to make possible the addition of alcohol above the level of the crystal glass without setting up convection currents.

After the films were mounted over the 0.1 mm holes of the diffraction camera specimen holders, they were placed under a bell jar and allowed to dry slowly in an alcohol atmosphere. When dry, the specimens became gray and puffy as in the case of transformer iron, but were much more transparent. The films proved to be too brittle, however, to remain intact over the 0.1 mm holes. This difficulty was overcome by the use of Resoglaz supporting films as described by Germer[11] and satisfactory diffraction patterns were obtained. Fig. 3 represents one of the patterns taken at 49,200 volts. There are 28 measurable rings on this plate. In most of the plates there were superimposed on the diffraction patterns three broad bands due to the Resoglaz. These made the estimation of the intensities somewhat more difficult.

In view of the interesting results obtained from the polycrystalline material, it was decided to examine the residue left from the dissolution of a single crystal of iron in ammonium persulphate. Accordingly, some laminae of a single crystal of iron were studied. Not the slightest trace of a grain boundary skin, or membrane, was observed. On the bottom of the petrie dish, however, there was a deposit of black specks resembling the black inclusions noted in the polycrystalline grain boundary membranes.

[11] L. H. Germer, private communication.

RESULTS

In Table II are given the diffraction data obtained from the grain boundary patterns. A comparison was made between these data and the crystal structure data for a number of compounds which were thought might be present in the grain boundary residue. This comparison showed that only two compounds, Fe_3C (iron carbide) and α FeOOH (goethite), could be identified. In Table II are given spacings and intensities for iron carbide based on the x-ray data obtained by Westgren[12] and Westgren and Phragmen.[13] The agreement between the grain boundary and the iron carbide data is sufficient to indicate the presence of iron carbide in the grain boundary residues. In the x-ray data of Westgren, the spacing 3.75 for the (101) planes was not ob-

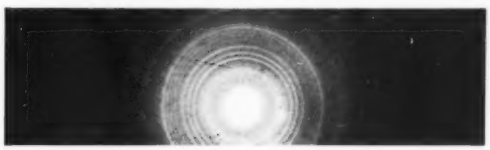


FIG. 3.

[12] A. Westgren, Jernkontorets Ann. **116**, 457 (1932).
[13] A. Westgren and G. Phragmen, J. Iron Steel Inst. **105**, 241 (1922).

TABLE II.

Fe_3C Iron Carbide					Grain Boundaries		αFeOOH Goethite						
	Westgren		Westgren and Phragmen		Average of 6 Plates		Goldsztaub		deJong		Cates		
hkl	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*	*I*	*hkl*
					5.01	*vw*	5.07	*vs*	4.85	*vw*			020
					4.50	*vw*			4.54	*vw*			
					4.24	*m*	4.28	*vs*	4.19	*vs*	4.04	*m*	110
101	3.75	—			3.77	*m*					3.75	*m*	
002	3.36	*vw*			3.30	*s*	3.41	*s*	3.31	*m*	3.30	*vw*	120
111	3.01	*vw*			2.98	*s*			2.96	*w*	2.95	*vw*	
					2.73	*w*	2.73	*vs*	2.71	*vs*			130
					2.64	*s*			2.57	*w*	2.62	*s*	021
020	2.54	*vw*					2.52	*vs*	2.48	*w*			040
112	2.38	*m*	2.39	*m*	2.39	*m*			2.44	*vs*	2.39	*s*	111
200	2.26	*m*	2.26	*w*	2.25	*m*	2.28	*s*			2.20	*w*	121
121	2.10	*s*	2.11	*m*	2.14	*m*	2.20	*s*	2.18	*m*	2.12	*m*	140
210	2.06	*s*	2.07	*m*	2.06	*w*							
022	2.02	*s*	2.04	*s*	2.02	*m*	2.03	*s*					131
103	2.01	*vs*											
211	1.97	*s*	1.98	*m*	1.96	*w*			1.92	*m*			
113	1.87	*m*	1.87	*s*	1.89	*w*			1.88	*vw*	1.87	*w*	
122	1.85	*s*											
212	1.76	*m*	1.76	*w*	1.78	*w*	1.79	*s*	1.78	*w*			141
									1.77	*w*			
004	1.68	*w*	1.69	*w*	1.70	*w*			1.71	*vs*	1.69	*s*	221
									1.68	*w*			240
221	1.61	*w*	1.64	*vw*	1.65	*m*	1.67	*s*	1.64	*w*			060
130	1.58	*m*	1.59	*w*	1.60	*m*	1.58	*vs*	1.60	*m*	1.58	*m*	151
131	1.54	*w*	1.55	*vw*	1.55	*m*			1.56	*s*	1.54	*s*	
114	1.50	*w*	1.51	*w*	1.48	*m*			1.50	*s*	1.49	*m*	
							1.44	*s*	1.45	*m*	1.44	*s*	112
311			1.42	*w*									
024	1.40	*w*			1.38	*w*	1.39	*m*	1.39	*w*			122
124	1.34	*w*											
231			1.34	*m*	1.36	*m*							
312	1.32	*s*			1.33	*m*	1.33	*vs*			1.34	*m*	132
							1.29	*s*			1.29	*w*	202
							1.27	*m*					212
232	1.26	*w*	1.26	*vw*			1.26	*s*					142
140	1.22	*s*	1.23	*m*			1.25	*w*					222
313	1.21	*s*	1.22	*m*	1.21	*m*							
233	1.16	*s*	1.16	*s*	1.15	*w*	1.14	*s*			1.12	*m*	242
142	1.14	*vw*	1.16	*s*									
400	1.12	*w*	1.13	*s*									
006	1.12	*m*	1.13	*s*									
331	1.11	*w*	1.11	*s*	1.11	*w*							
314	1.09	*m*	1.10	*w*	1.10	*vw*							
411	1.09	*m*	1.09	*w*			1.08	*s*					252
242	1.05	*w*	1.06	*m*									
412	1.04	*w*	1.05	*vw*	1.04	*w*							

Letters used in describing the intensities are:
vs—very strong
s—strong
m—medium
w—weak
vw—very weak.

served, but his computation for the intensity showed that there was a faint reflection from these planes. It is, therefore, possible that the 3.79 spacing of the grain boundary data may be due in part to the reflection from the (101) planes of iron carbide.

The spacings and reflection intensities for α FeOOH, based on the x-ray data of Goldsztaub,[14] deJong[15] and Cates[16] are given in Table II. By comparing the combined findings of these three authors with the spacings obtained for the

[14] M. S. Goldsztaub, Bul. Soc. Fran. Mineral **58**, 6 (1935).
[15] W. F. deJong, Natuurw. Tijdschrift. **12**, 69 (1930).
[16] J. Cates, Trans. Faraday Soc. **29**, 817 (1933).

grain boundary residue it is seen that the agreement is such as to indicate the presence of αFeOOH. It is somewhat surprising that there was no spacing in the grain boundary data to correspond with the 2.52 spacing reported by Goldsztaub and the 2.48 spacing by deJong for αFeOOH, and with the 2.54 spacing for iron carbide. There is, however, lack of agreement in the literature with regard to the reflections from the (040) planes of αFeOOH since Goldsztaub finds that the reflection is strong, deJong that it is weak, and Cates gives nothing.

Discussion and Conclusions

An examination of the data in Table II shows that practically all the spacings found in the grain boundary data may be accounted for either by the presence of iron carbide, or by the presence of αFeOOH. It is therefore impossible to determine whether one of these materials exists by itself or whether both are present. Further analysis, either by the combination of electron and x-ray diffraction, or by some other method, will be necessary to make this determination.

The presence of iron carbide in the grain boundary residues would be expected. It is insoluble in ammonium persulphate, and the initial heat treatment of the iron laminae was such as to cause the iron carbide to gather at the grain boundaries.

The presence of α FeOOH in the grain boundary residue would raise the question as to whether the hydrated ferric oxide is present originally in the grain boundaries, or whether it is formed by a chemical reaction accompanying the dissolution of the iron laminae in the persulphate solution. Our knowledge of the impurities in iron leads one to suspect that αFeOOH does not occur in the grain boundaries but is formed by some chemical reaction during the process of dissolution of the iron and of washing the residue. Two ways in which it might be formed are: (1) as a result of a chemical reaction of the dissolved iron with ammonium persulphate, or (2) as a result of a chemical reaction of some grain boundary constituent, such as an oxide of iron, with ammonium persulphate, oxygen and water. This is a problem for a special investigation and work on it is now in progress.

The method of investigation of grain boundary materials which involves the dissolution of the metal grains, does not afford a complete analysis. Materials in the grain boundaries may be changed chemically, or be completely dissolved by the solvent. For example, free copper, present in the grain boundaries of iron, could not be detected by this method due to its dissolution in the persulphate solution. Moreover amorphous material would not be detected by electron diffraction. The method, nevertheless, makes possible important contributions to the study of grain boundaries since the presence of crystalline materials in the residues may be detected.

The authors hope to continue the work by supplementing electron diffraction with x-ray diffraction methods, particularly in the case of heavier films as found in transformer iron. It is proposed to study other metals in addition to iron and if possible to pretreat some of the metal specimens in a hydrogen furnace for purification.

Acknowledgments

The writers wish to express their gratitude to the Reading Iron Company, Reading, Pennsylvania, for the assistance of their chief chemist, N. S. Matheson, who made the chemical analyses and the microphotographs shown in Figs. 2(a) and 2(b); and to Girard College, Philadelphia, Pennsylvania, for the loan of high voltage equipment. The first of the authors also gratefully acknowledges special grants of the Faculty Research Committee of the University of Pennsylvania, and of the Grants-in-Aid Committee of the National Research Council. These grants were used in part to secure apparatus and materials necessary for the experimental work.

A Study of Melting of the Mononitrophenols at High Pressure

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The melting of the mononitrophenols has been studied over a pressure range of 4,000 kg/cm² by separate application of a piston displacement and a new dynamic method. By the dynamic method, the procedure was to observe the sudden change of temperature difference as the nitrophenol underwent melting with change of pressure. Comparison of results obtained by the two methods indicate close agreement for the pressure-melting temperature data of ortho- and metanitrophenol which have not been studied previously over the present pressure range. Application of the dynamic method is compared briefly with that of the piston displacement method in respect to melting and polymorphic transitions of solids at high pressure.

MELTING phenomena at high pressure have been investigated by Bridgman[1] who has exploited extensively the piston displacement or equilibrium method to obtain pressure-volume data at constant temperatures. It is well known by his thorough studies that these data are sufficient to allow a complete treatment of the thermodynamics of melting. A number of other investigators[2] have determined the pressure-temperature relations of melting by use of a nonequilibrium or dynamic method.

The usual procedure by the latter method has been to measure the temperature of the transition by means of a thermocouple, one junction of which was imbedded in the substance in the pressure chamber and the other used with it differentially under the same pressure conditions, or kept at constant temperature at atmospheric pressure. The temperature of melting could be determined then from an ordinary time temperature curve obtained at constant pressure. While application of this method has a definite field of usefulness in the mapping of pressure-temperature relations, it is necessary to make separate dilatomic measurements to obtain the change of volume with change of state, a quantity necessary for computation of the latent heat.

This paper reports new pressure-temperature data that have been measured for the melting of the nitrophenols by use of a dynamic method, and compares these data with similar ones given by application of the piston displacement method. Paranitrophenol has been investigated by Bridgman[3] and orthonitrophenol over a low pressure range by Hulett,[4] but apparently the meta form has not been investigated previously. The nitrophenols used by the authors had been obtained originally from Eastman and were further purified by recrystallization from alcohol until satisfactory melting points were observed. The melting points at atmospheric pressure are given in Table I.

Experimental Detail

The pressure apparatus consisted of two independent assemblies which were similar in many respects. Pressure was generated by the conventional Bridgman type pump and intensifier in both cases, the pressures being measured by the change of resistance of a manganin coil whose pressure coefficient was known. The test chambers, however, were somewhat different, necessitated by the difference in experimental method.

The test chamber used in the dynamic method was a heavy steel, right cylinder that was connected directly to one intensifier and pump. The pressures obtained in this assembly were limited, consequently, to about 5000 kg/cm², the maximum pressure obtainable with the intensifier. A hole, coaxial with the long axis of the cylinder, was drilled part way into it to hold the test cell which contained nitrophenol. A three

[1] P. W. Bridgman, *Physics of High Pressure* (Macmillan 1931), Chap. 7.
[2] John Johnston and L. H. Adams, Am. J. Sci. **31**, 501 (1911); R. E. Gibson, J. Phys. Chem. **32**, 1197 (1928); Gustav Tammann, *The States of Aggregation* (D. Van Nostrand 1925), p. 80.
[3] P. W. Bridgman, Phys. Rev. **6**, 16 (1915).
[4] G. A. Hulett, Zeits. f. physik. Chemie **28**, 629 (1899).

terminal, threaded plug provided external electrical connections to the cell and closed the chamber. Smaller openings on the side of the cylinder which connected to the central chamber provided means for connecting to the intensifier, and inserting the plug which carried the manganin pressure coil. Since the pressure coil was in the test chamber which was surrounded by baths of various temperatures, it was necessary to have information about the temperature variation of the pressure coefficient. While it would have been simpler to keep the pressure coil at constant room temperature by using an additional chamber, one was not available at the time and it was necessary to make the temperature correction. This was done experimentally at each temperature without difficulty.

The test cell consisted of a U-shaped tube made from soft glass tubing of about 5 mm diameter through which a copper-copel thermocouple was strung; after filling with liquid nitrophenol, the tube was inverted and its ends submerged in mercury which was contained in glass tubes of slightly larger bore. By this procedure the nitrophenol was exposed to the pressure of the system but separated from the kerosene which was used to transmit the pressure. The complete test cell was suspended vertically from the three-terminal plug and the thermocouple junction connected differentially with one of two other junctions, each of which could be inserted independently in the circuit by means of a selector switch. These two junctions were placed in the pressure chamber and in the external bath, respectively, thus enabling the temperature difference between the substance in the cell and either the bath or the inside of the pressure chamber to be measured when the thermocouple circuit was suitably connected to a galvanometer. A Leeds and Northrup type R galvanometer of low resistance was used for these measurements. The assembled test cell as it was connected to the three terminal plug is shown in Fig. 1. The copper-copel couple had a comparatively large thermal e.m.f. for a unit difference of temperature, 0.0616 mill v/°C, and when used differentially temperature differences of 0.03°C were easily detected.

The test chamber of the second assembly was also a heavy steel cylinder that was connected

FIG. 1. Assembled test cell for measurements by dynamic method.

at one end to a Bridgman type press[5] and its other closed by a pressure plug. This cylinder had a similar coaxial chamber into which was inserted a steel tube that had been filled previously with melted nitrophenol. Previous tests had shown, meanwhile, that it was not necessary to separate the nitrophenol from the kerosene of the pressure system, hence the tube and contents were exposed to the pressure transmitting liquid. It will be recalled that melting at a certain fixed temperature is observed when a break appears in the curve of pressure versus piston displacement. Measurements of this kind are made when the substance is in thermal equilibrium with the bath. The pressure coil of this apparatus was maintained at room temperature during the tests, thus eliminating temperature corrections. While this assembly could be used at very high pressures, none higher than 4000 kg/cm^2 was used, principally because these tests were made to check the results obtained by use of the dynamic method

[5] Reference 1, p. 42.

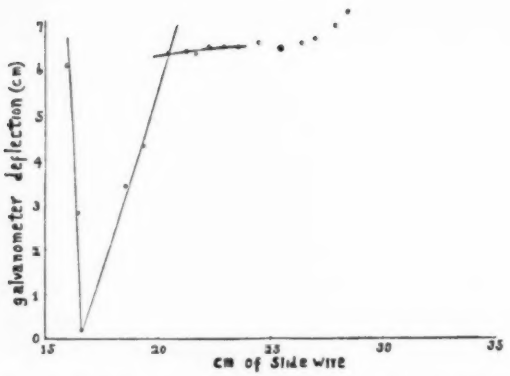

FIG. 2. Melting curve of metanitrophenol at 112°C, cm of slide wire against galvanometer deflection; these are proportional to the pressure and temperature difference, respectively. Melting began at 840 kg/cm².

rather than to extend the melting curves to higher pressures which would have required higher bath temperatures.

The baths surrounding the test chambers of both assemblies were either water or oil that were thermostatically controlled to within a few hundredths of a degree centigrade. A mercurial thermometer which was later checked against one calibrated by the National Bureau of Standards indicated the bath temperatures. The effect of pressure on the thermoelectromotive force of the couple used with the first assembly is so small that it could be neglected without serious error.

The procedure adopted for the nonequilibrium or dynamic method was to observe the sudden change of temperature difference between the nitrophenol and the interior of the pressure chamber as the nitrophenol underwent melting with change of pressure, the bath temperature being fixed during the experiment. This procedure differed essentially from the dynamic method already described, but Tammann[2] mentions that the variation of the thermoelectric current with pressure has been used to detect the melting of Glauber's salt. In practice, the bath when raised to a certain temperature was allowed to stand until the differential thermocouple indicated that the substance at atmospheric pressure had reached the temperature of the bath to within a few tenths of a degree. This required about an hour and further time was not spent to obtain equilibrium because the method of experiment was a nonequilibrium one.

Increase of pressure then produced a temperature rise in the nitrophenol, the amount depending on the rapidity and magnitude of the pressure change. Since the process was neither strictly adiabatic nor isothermal, one cannot speak of the temperature rise or heat of compression with exactness. It was interesting to discover that the pressure-temperature curves were not similar for increase and decrease of pressure but these thermal differences, while interesting, did not affect the observance of melting. Fig. 2 illustrates a typical curve obtained with decreasing pressure for metanitrophenol at a temperature of 112°C; a break of large magnitude appeared when the substance began to melt. The precision of the method depended largely on the magnitude of pressure change with time; in these experiments the melting points were located by using pressure differences of about 60 kg/cm² over periods varying from 2 to 6 minutes. With such slow rates all of the heat was not dissipated between pressure changes and the inside of the pressure chamber was as much as 1° above or below the temperature of the bath. This caused no trouble in computation as the bath temperatures were always known as well as the temperature differences. Since it is impossible to superheat a crystalline phase with respect to the liquid, the melting curves were observed rather than the freezing ones.

The actual melting points were obtained by this method by plotting large scale pressure-temperature difference data of the type represented by Fig. 2 and then estimating the pressure at which melting began. It appeared that pressures could be estimated to within ±10 kg/cm². The recorded bath temperature was corrected by the temperature difference when melting began, as given by the differential thermocouple, to give the temperature of melting.

TABLE I. *Pressure-temperature relations for ortho- and metanitrophenol.*

PRESSURE (kg/cm²)	MELTING TEMPERATURE (°C) ORTHONITROPHENOL	METANITROPHENOL
1	46.0	95.7
1000	68.2	115.0
2000	89.0	133.9
3000	109.9	151.5
4000	130.6	

The piston displacement method of determining the melting curves requires little explanation. The piston displacements, taken when the pressure and bath were in thermal equilibrium, were measured with micrometers. The readings were reproducible to within 0.001″. Here also the data were taken with decreasing pressures. A large scale graph of pressure against piston displacement enabled the writers to detect melting at the change of slope with considerable accuracy, The change of volume on melting of the nitrophenols was sufficiently large to be measured easily but these data are not reported for two reasons: first, the high pressure chambers being new had not been sufficiently seasoned to allow accurate determinations of the change of volume which can be computed accurately by this method only when several corrections are made experimentally; secondly, since only a few tests were made for the purpose of checking the accuracy of the first method, these would have given insufficient data on the change of volume to allow accurate computation of the latent heat of melting over the experimental range for which pressure-temperature data were obtained. Inspection of the data available for the approximate change of volume, and for the pressure-temperature relations, showed that no salient differences in the thermal behavior at melting were to be expected for the three isomers, hence a detailed study of the volume relations has not been undertaken since the completion of these experiments.

Discussed Results

The pressure-temperature data of ortho- and metanitrophenol are given at pressure intervals of 1000 kg/cm² in Table I. Fig. 3 represents the results graphically, and shows the experimental points taken according to both methods. The data obtained by the use of both methods agreed to such an extent that, within the errors of the experiments, an average curve could be drawn from both sets of p-t points as the best representation of the results. The data of Table I were obtained from such large scale, average curves.

The curve for paranitrophenol of Fig. 3 was obtained by application of the dynamic method

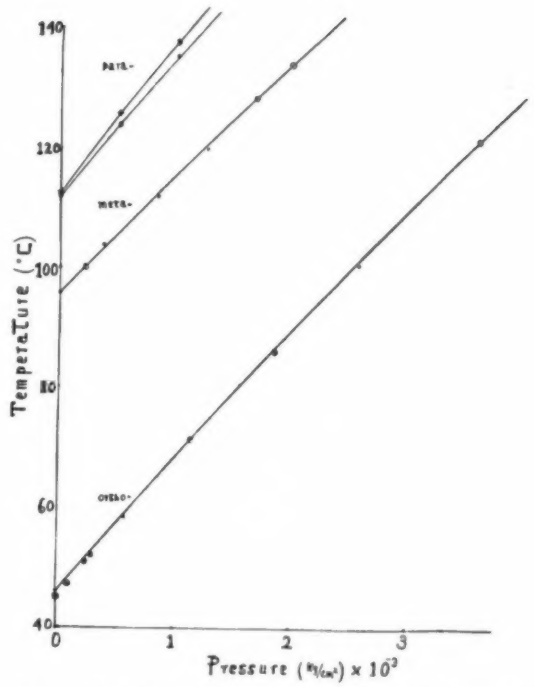

Fig. 3. Melting curves for ortho-, meta- and paranitrophenol. The cross represents Bridgman's points; the cross within the circle, Hulett's; black dot, authors' dynamic; circle, authors' equilibrium points.

alone. The results were not comparable with Bridgman's since the writers' paranitrophenol was less pure, as indicated by a lower melting point at atmospheric pressure. Similarly, it is apparent that Hulett's orthonitrophenol was less pure than that used in the present investigation. Preliminary tests with less pure orthonitrophenol showed that not only was the melting point lowered but that the slope of the melting curve varied with purity; the dynamic method is not capable of dealing with impure substances as well as the piston displacement method.

The close agreement of the results by the two different methods gives a satisfactory check on the general accuracy and indicates that reliable data can be obtained by application of the dynamic method described in this paper. The writers are not aware of a similar study which has compared equilibrium and nonequilibrium methods. It is interesting to note that the greatest deviation of a single point from its average curve amounted to 6 percent for metanitrophenol; for orthonitrophenol a similar deviation amounted to 3 percent. Inspection of Fig. 3

indicates that the latter figure is probably more representative of the general accuracy of the results.

On comparing the two methods of this paper as regards uniformity of procedure and completeness of data, the piston displacement method is to be preferred for studying melting at high pressure. For the observance of polymorphic changes in solids, it seems unlikely that the dynamic method of this paper could be used satisfactorily to fix transition pressures since the procedure would tend to widen regions of instability. However, for a rapid survey of possible solid-solid transitions, the dynamic method should prove to be useful for preliminary studies.

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The Phase Diagram of Water to 45,000 kg/cm²

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ABOUT two years ago I found that ice VI is transformed into a new high pressure modification, ice VII, at pressures between 20,000 and 25,000 kg/cm². Although various incidental references have been made to this in print I have not yet published any numerical data on the transition because I wanted at the same time to present data for the melting curve of VII and for the compressibility. Values of these have now been obtained and are given in the following. The melting curve has been carried up to 190° and 40,000 kg/cm², and the parameters for it are fairly good. The compressibilities are much more difficult to obtain, and I have only rough values for the compressibility of VII. It would probably be possible to considerably improve the compressibility measurements with a new apparatus now under construction. However, I did not want to hold up publication of the data already at hand indefinitely until the new apparatus could be made to function, but I intend to publish later improved and more extensive compressibilities if it proves possible to obtain them. Because of the interest in all the properties of water it has seemed desirable to present these results in a paper by themselves, and in a journal somewhat more accessible than that in which most of my results for other phase diagrams have been published.

The new technique by which it has been possible to considerably extend my previous pressure range and to measure the parameters of polymorphic transitions has been sufficiently described in previous papers.[1] By a refinement of the same technique it is also possible to obtain rough values for compressibilities. It is, however, much more difficult to get a good value for compressibility at high pressures than it is to get the volume change at a transition, because there are various corrections for distortion and creep which do not enter into the measurement of the volume change at a transition. I do not propose to discuss here the various precautions which have to be taken in measuring compressibility, but shall reserve this for another paper, probably in *Proceedings of the American Academy of Arts and Sciences*, in which I shall give the compressibility of a number of substances. It is sufficient here to remark that fairly consistent compressibilities can be obtained for the more compressible substances, but that the compressibility of the ordinary metals must be determined by some other method.

The chief technical difficulty in measuring water is the leak which occurs when it is in the liquid phase; this leak must be avoided if accurate values of the volume change on melting are to be obtained. The method adopted after a number of trials was to seal the water into a heavy lead capsule with Wood's metal. Even this is not entirely satisfactory, but the walls of

[1] P. W. Bridgman, Phys. Rev. **48**, 893 (1935); Proc. Am. Acad. **72**, 46 (1937).

the capsule are likely to be pulled apart after pressure has been applied and released because of the large volume changes, the volume under 45,000 being of the order of 0.6 of the initial volume. Half a dozen different set-ups were made, terminated by leak or by rupture of the apparatus, in getting the final results. The actual pressure on the carboloy piston was pushed beyond 50,000 in exploring for still other possible modifications and in measuring the compressibility of VII at room temperature, but friction, which could be calculated from the difference between readings with increasing and decreasing pressure, cut down the actual maximum pressure inside the apparatus to the neighborhood of 45,000. No other modification of the solid was found up to this pressure.

The experimental results are collected in Figs. 1 and 2, and the numerical values of the various parameters in Table I. The triple point L–VI–VII is at 22,400 kg/cm² and 81.6°; the triple point parameters are included in the table. The various curves were so adjusted as to satisfy the various additive relations at the triple point. The fact that it was possible to do this without doing violence to the independently determined parameters on the various transition lines, as shown in Fig. 1, is presumptive evidence that the values cannot be far wrong. The parameters on the melting curve of VI were determined at only a single point. Previous measurements had been made to a maximum temperature of 76.4° on the melting curve and to a maximum temperature of 55.5° for the change of volume. The parameters given in the table were obtained by fitting the new single point in smoothly with those previously determined, also taking due account of the additive relations at the triple point. In Fig. 1 the previously determined temperatures on the melting curve are indicated by crosses; these are seen to lie consistently with the point now found; this incidentally confirms the validity of extrapolating the manganin gauge measurements from 13,000 to 20,700 in the previous work.

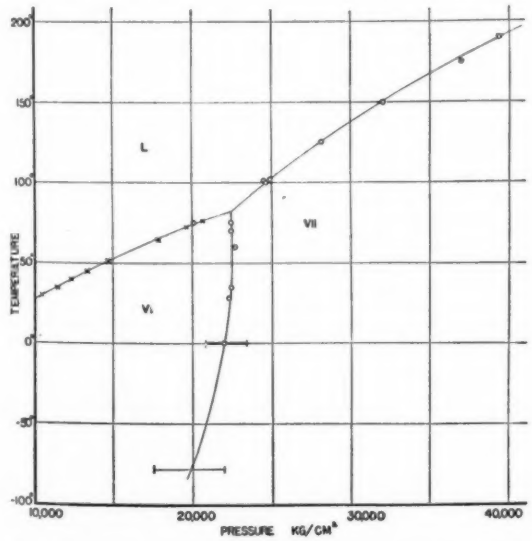

FIG. 1. The phase diagram of water in the region of the new high pressure solid. Crosses are determinations on the melting curve of VI made in 1912.

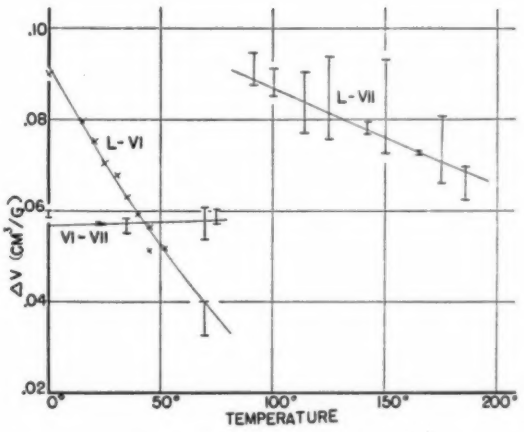

FIG. 2. The volume changes for the several high pressure transition in the water system. The crosses represent data obtained in 1912.

Several trials were made for the compressibilities of the various phases, but with indifferent success. Consistent values were not obtained for the compressibility of liquid or of VI. The two best runs gave fairly consistent values for the compressibility of VII, however. Between 20,000 and 45,000 kg/cm², two independent measurements gave for the total proportional volume change 0.041 and 0.037 cm³/g, mean 0.039 cm³/g. It was also possible to definitely establish the normal decrease of compressibility with rising pressure; the mean compressibility in the range 45,000–50,000 is about three quarters of that in the range 20,000–25,000. Although consistent values for the compressibility of VI were not obtained, it is highly probable that my

TABLE I. *Transition parameters of the high pressure forms of water.*

PRESSURE kg/cm²	TEMPERATURE °C	$\frac{d\tau}{dp}$	ΔV cm³/g	LATENT HEAT kg cm/g	LATENT HEAT cal./g	$p\Delta V$
			VI–liquid			
15,000	52.5	0.00486	0.0508	3,400	79.7	762
16,000	57.2	460	478	3,430	80.4	764
18,000	66.0	412	424	3,490	81.8	762
20,000	73.8	370	376	3,520	82.5	753
22,000	80.8	330	335	3,590	84.1	737
22,400	81.6	324	330	3,610	84.7	738
			VII–liquid			
22,400	81.6	.00892	.0910	3,620	84.7	2,040
24,000	95.3	796	879	4,060	95.1	2,110
26,000	110.3	718	847	4,530	106.2	2,200
28,000	124.1	670	817	4,840	113.4	2,290
30,000	137.1	634	789	5,100	119.5	2,360
32,000	149.5	600	763	5,370	125.9	2,440
34,000	161.1	567	738	5,650	132.4	2,510
36,000	172.1	536	715	5,940	139.2	2,580
38,000	182.5	507	694	6,220	145.8	2,640
40,000	192.3	479	674	6,550	153.5	2,700
			VII–VI			
19,680	−80.0	.0278				
20,370	−60.0	0303				
21,000	−40.0	0339				
21,550	−20.0	0400				
22,000	0.0	054	.0567	287	6.7	1,250
22,250	20.0	118	570	142	3.3	1,270
22,350	40.0	286	573	63	1.5	1,280
22,390	60.0	1.000	576	19	.5	1,290
22,400	80.0	∞	580	0		1,300
22,400	81.6	∞	580	0		1,300

previously published values were too high.[2] It is also highly probable that at the triple point the compressibility of VII is a few percent greater than that of VI in spite of its smaller volume; this state of affairs is not at all unusual. At 50,000 kg/cm² and room temperature the volume of VII is approximately 0.60 cm³/g. This value is indicated both by a summation of the changes of volume occurring during the several phase changes and the compressions of the several pure phases, and also by a direct measurement of the total over-all change of volume.

In general comment on the results, one may notice in the first place that the decrement of volume when the liquid freezes to VII at the triple point VI–VII–L at 22,400 kg is practically the same as the volume decrement when liquid freezes to VI at the triple point V–VI–L at 6380 kg, being 0.0910 against 0.0916 cm³/g. The decrease along the melting line of the volume decrement L–VI is very large, dropping from 0.0916 at the lower triple point to 0.0330 at the upper triple point. This in itself might perhaps be taken as a suggestion of the imminence of a new phase. Along the melting line of VII the decrease of the volume decrement L–VII is at a much lower rate, so that an application of the same argument would not demand the speedy appearance of yet another modification of the solid. It was a surprise to me that the change of volume of the liquid on freezing to VII at the triple point at 22,400 was so high; one might perhaps expect the volumes of the different phases to be squeezed down into a closer approach to equality at such high pressures.

The curvature of the melting curve of VII is in the normal direction. On the other hand, there is an abnormally great increase in the latent heat. This increase is so much greater than the increase in absolute temperature that the entropy difference between liquid and solid increases by more than 40 percent from 22,400 to 40,000 kg on the melting curve. Not only does the entropy difference between liquid and VII increase at high pressures along the melting curve, but the energy difference also increases, as may be seen from the table by subtracting the values of $p\Delta v$ from the latent heat. Extrapolation of this melting line therefore certainly gives no indication of either an approaching maximum or of a critical point.

As far as the two solids VI and VII are concerned, the normal relations were found. The transition runs with very high velocity at temperatures near the triple point, but becomes rapidly less at lower temperatures. Even 160° below the triple point, however, the velocity is still very appreciable outside the limits of indifference indicated in Fig. 1.

I am indebted to my assistant, Mr. L. H. Abbot, for many of the readings, and for financial assistance to the Rumford Fund of the American Academy of Arts and Sciences.

[2] P. W. Bridgman, Proc. Am. Acad. **47**, 535 (1912).

On the Correlation of Fluidity Curves with Freezing Point Curves in Binary Systems

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Binary systems which form crystalline compounds nearly always exhibit negative deviations from the ideal laws for liquid solutions of the type $G=N_1G_1^0+N_2G_2^0$, where N is mole fraction and G may be volume, heat content, vapor pressure or fluidity. The deviations from ideality are often approximately parabolic functions of the molecular composition with the maximum deviation at or near 50 mole percent. In the case of fluidity this type of deviation is observed whatever the composition of the crystalline compound or compounds which occur in the system, leading to the conclusion that there is no correlation between the position of the maximum fluidity deviation and the composition of the crystalline compounds indicated by the freezing point curve. The bearing of this conclusion on the question of compound formation in the liquid is discussed.

BINARY systems which exhibit either maxima or binary reaction points[1] on the freezing point curves are said to form crystalline compounds, and it is usually presumed that the compound (or compounds) is also present to a greater or less extent in the liquid phase. Liquid solutions in such systems nearly always exhibit negative deviations from all the ideal mixture laws:

$$V<V_{\text{ideal}}=N_1V_1^0+N_2V_2^0 \text{ (contraction)},$$
$$H<H_{\text{ideal}}=N_1H_1^0+N_2H_2^0 \text{ (evolution of heat)},$$
$$p<p_{\text{ideal}}=N_1p_1^0+N_2p_2^0,$$
$$\phi<\phi_{\text{ideal}}=N_1\phi_1^0+N_2\phi_2^0,^2$$

where V=volume, H=heat content, p=vapor pressure, ϕ=fluidity (reciprocal of viscosity), N=mole fraction, and the superscript zeros refer to the pure components.

The deviations from these ideal laws are usually approximately parabolic functions of the molecular concentration, and the deviation-composition curves are frequently approximately of the type shown in Fig. 1. Curves of this type for heat of mixing or for volume change on mixing are familiar,[3] and similar curves for vapor pressure deviations can be constructed from vapor pressure data in the literature. Fluidity deviation curves of this type will be given in this paper for the first time, and it will be seen (Figs. 3–14) that these curves are often nearly perfect parabolas, and more frequently so than are curves of heat of mixing and of volume change on mixing.

These deviation-composition curves can often be approximately represented by a function

$$\Delta G=kN_1N_2,$$

which is the equation of a parabola symmetrical about the line $N_1=N_2=\frac{1}{2}$, the constant k being four times the ordinate of the maximum point. Biron[4] first applied this equation to volume changes on mixing, and later it was applied to heats of mixing by Baud.[5] A slightly variant form has recently been given a theoretical deduction for the heat of mixing in regular solutions.[6]

The discussion so far has concerned only negative deviations from the ideal laws. The opposite behavior, i.e., positive deviations from all the ideal laws, is the more common case and

[1] The term binary reaction point is the more precise term which has been used in the literature recently to designate the melting point of an incongruent melting compound, the older term transition point being reserved for discontinuities in the freezing point curve due to a transition in one of the pure components. Fig. 10 illustrates both these types of discontinuities.

[2] The ideal mixture law for fluidity given above will be demonstrated both theoretically and experimentally in a forthcoming paper. A brief justification follows. It has been shown (Eyring, J. Chem. Phys. **4**, 283 (1936) and Ewell and Eyring, J. Chem. Phys. **5**, 726 (1937)) that flow can be considered as a unimolecular rate process in which the activation energy takes the form of providing a hole for the molecule to flow into. Flow in a binary mixture of liquids can be considered as analogous to two unimolecular chemical reactions which yield the same product proceeding simultaneously in the same vessel. This concept leads directly to the ideal law $\phi=N_1\phi_1^0+N_2\phi_2^0$. As is the case with the other ideal laws, strict adherence is rarely observed.

[3] See Timmermans, *Les Solutions Concentrees* (Masson et Cie., Paris, 1936).

[4] Biron, J. Russ. Phys.-Chem. Soc. **41**, 569 (1909).

[5] Baud, Bull. soc. chim. 4, **17**, 329 (1915).

[6] Hildebrand and Wood, J. Chem. Phys. **1**, 817 (1933); Vold, J. Am. Chem. Soc. **59**, 1515 (1937).

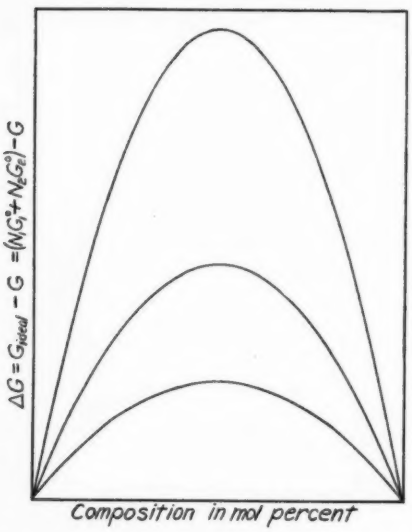

FIG. 1. Type of curves of the negative deviation of a property from its ideal value as a function of composition, where G may be volume, heat content, vapor pressure or fluidity.

is exhibited by nonaqueous solutions of non-electrolytes, which have only a eutectic on the freezing point curve, e.g., benzene and carbon disulfide, hexane and ether, carbon tetrachloride and ethyl alcohol, etc. The deviations for these mixtures also have a parabolic form, but in the opposite sense from that shown in Fig. 1 since the observed values of the properties are greater than the ideal values. This type of mixture will be considered in the forthcoming paper mentioned in reference 2, and also aqueous solutions which occupy an entirely separate category.

The viscosity of binary mixtures which form crystalline compounds has been considered at some length by other writers.[7] The leading idea has been to interpret the frequently observed viscosity maxima in terms of compound formation in the liquid. The matter was complicated by the fact that the maximum was practically never at the composition of the compound (or of one of the compounds) indicated by the freezing point curve, and also the position of the maximum usually shifted with temperature. Furthermore,

[7] Thorpe and Rodger, J. Chem. Soc. **71**, 360 (1897); Dunstan, ibid. **85**, 817 (1904); **87**, 11 (1905); Thole, Mussel and Dunstan, ibid. **103**, 1108 (1913); Tsakalotos, Bull. soc. chim. [4], **3**, 234 (1908); Bramley, J. Chem. Soc. **109**, 10, 434, 469 (1916); Bingham, *Fluidity and Plasticity* (McGraw-Hill Co., New York, 1922); Kurnakov, Zeits. f. anorg. allgem. Chemie **135**, 81 (1924); Hatschek, *Viscosity of Liquids* (G. Bell and Sons, London, 1928).

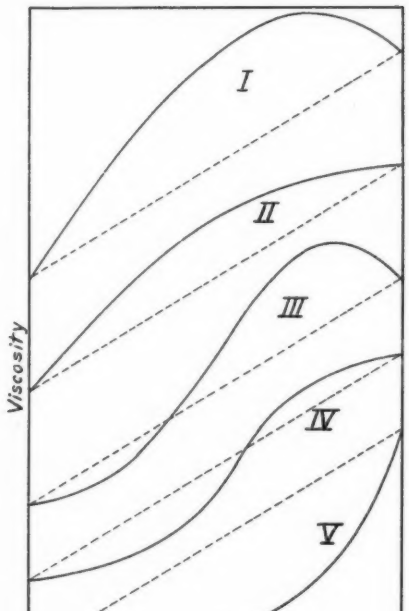

FIG. 2. Types of viscosity composition curves given by binary systems which form crystalline compounds, either congruent or incongruent melting.

in other cases where the freezing point curve showed the formation of crystalline compounds there were no maxima at all observed in the viscosity curves, and sometimes the deviation from linear viscosity was actually negative, and sometimes an inflected curve with both positive and negative deviations was observed. Five types of viscosity-composition curves observed are shown in Fig. 2.

According to the view stated earlier, it is the fluidity that is the significant additive property, and if the fluidity is plotted against the molecular concentration, these five types of viscosity curves all give the same type of fluidity curve: uniformly negative deviations from linearity, with or without a minimum in the fluidity curve. The presence or absence of a minimum is of no significance since it is the deviation from ideal that is important, and if the fluidity deviations are plotted against the molecular concentration, fairly symmetrical parabolas result in all cases. This is illustrated in Figs. 3–14. The bottom curve in each figure is the freezing point curve, next the viscosity curve, next the fluidity curve,

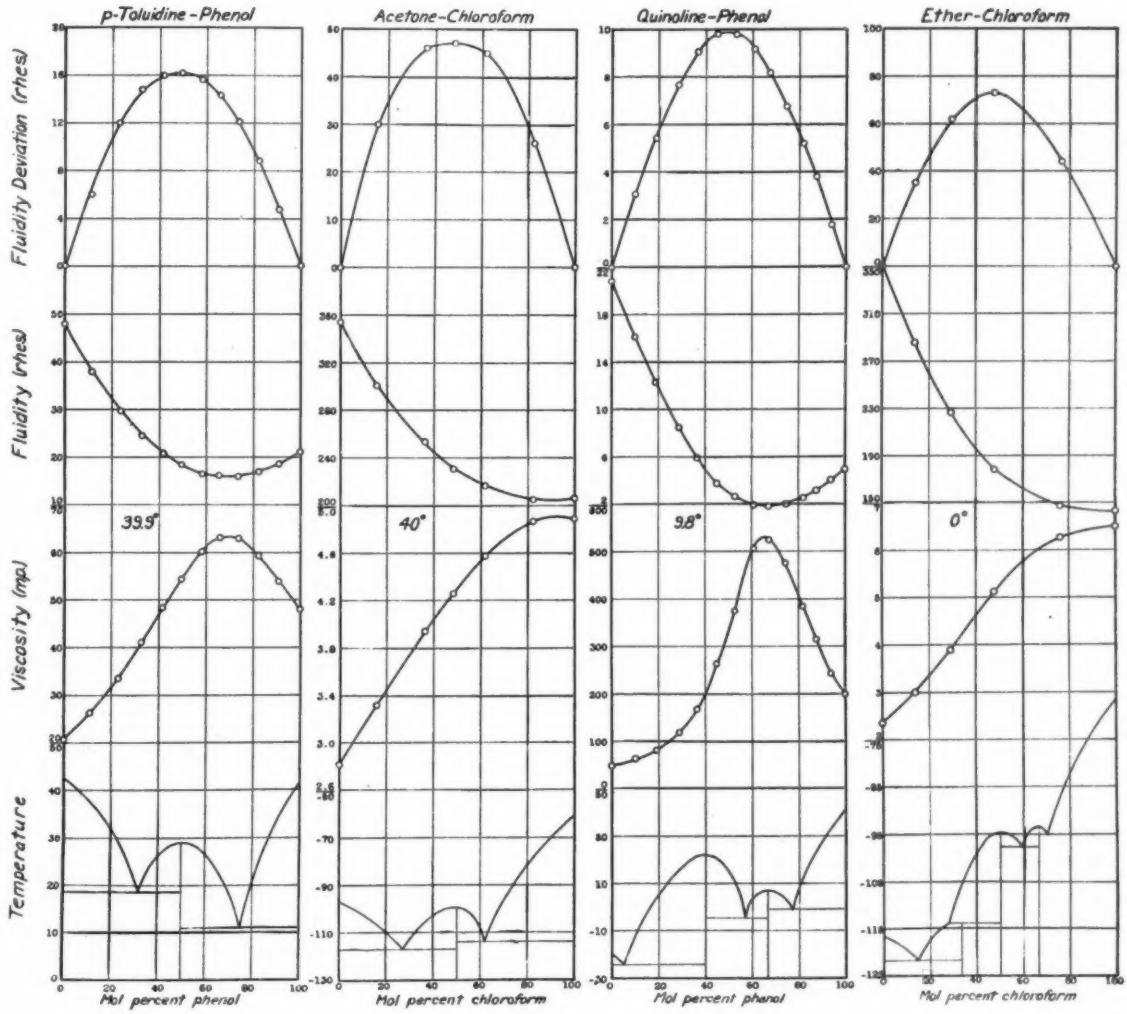

FIG. 3. FIG. 4. FIG. 5. FIG. 6.

and at the top the fluidity deviation curve. It should be noted that the absolute fluidity deviation in rhes (reciprocal poises) is plotted, and not a fractional or percentage deviation.

Figures 3–5 have viscosity curves of type I, Fig. 6 of type II, Figs. 7–8 of type III, Figs. 9–10 of type IV, and Figs. 11–12 of type V. The viscosity curve in Fig. 13 is the trivial case of a straight line. The phase boundaries (not showing solid solutions) have been sketched in under the freezing point curves just to show the compound compositions better. Several types of phase diagrams have been included in the examples: single compound of 1 : 1 composition, single compound of other than 1 : 1 composition, several compounds in the same system, and both congruent and incongruent melting compounds. The temperature of observation is given in the space between the viscosity and fluidity curves, and it is seen that part of the liquidus is often higher than this temperature, showing supercooling, especially in mixtures containing phenols. For nearly all these mixtures viscosity data were available at several temperatures, but only one temperature is given in each figure, since the general features of the curves were similar and little was to be gained from the extra drafting involved. The data from which the figures were drawn were taken from various authors (largely those of reference 7) and are all contained in the

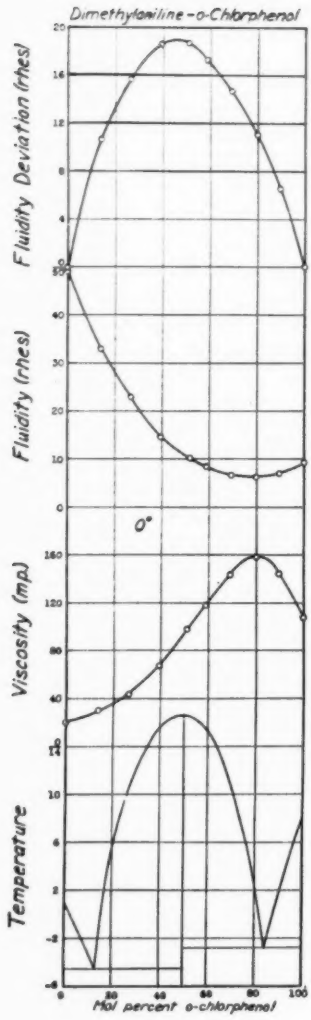

FIG. 7.

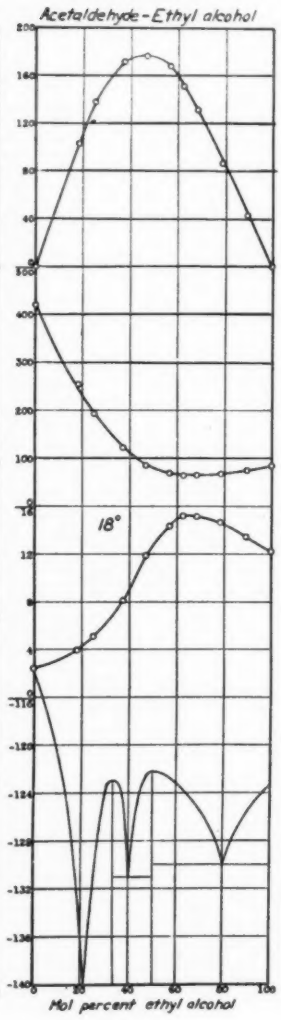

FIG. 8.

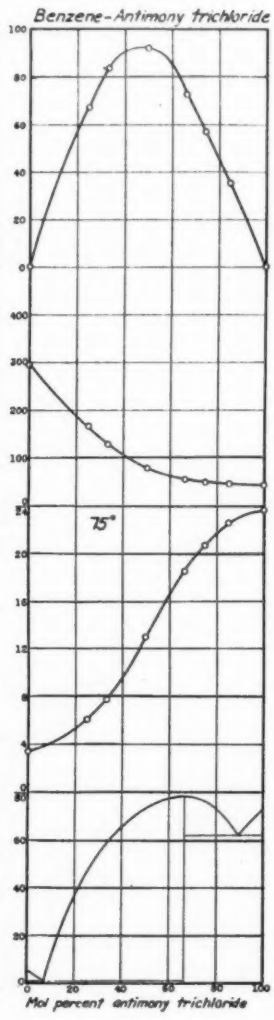

FIG. 9.

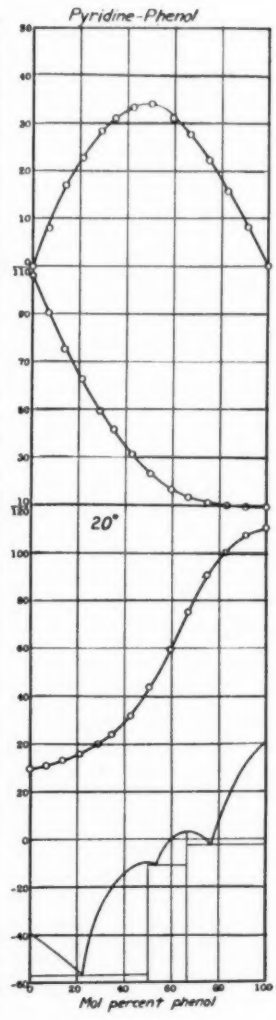

FIG. 10.

International Critical Tables, except the freezing point data for the systems acetone-carbon tetrachloride, benzene-carbon tetrachloride, and acetone-chloroform.[8]

Numerous examples of each of the five types of viscosity curves could be given, but the figures illustrate all the essential features, and any conclusions based on these examples can be considered as being supported by still others. Type V had been particularly troublesome to explain, but the apparent anomaly is clear when it is seen that ***both*** viscosity and fluidity curves deviate negatively from linearity. Kurnakov[7] studied two cases of type V, naphthalene with *m*-dinitrobenzene and with *s*-trinitrobenzene, each of which form 1 : 1 compounds, and Hatschek[7] makes particular mention of these apparently anomalous cases. However, the fluidity curves for both these mixtures show negative deviations as would be expected.

The positions of viscosity maxima not only shift with temperature, but the maxima may disappear altogether, and the type of curve change from one temperature to another. For instance, the system pyridine-*p*-cresol gives a viscosity curve of type V at 0, 10, 20, 30°, type IV at 40°, type III at 60, 80, 110°, and dimethylaniline-*o*-chlorphenol gives a curve of type III at

[8] Wyatt, Trans. Faraday Soc. **24**, 429 (1928); **25**, 43 (1929).

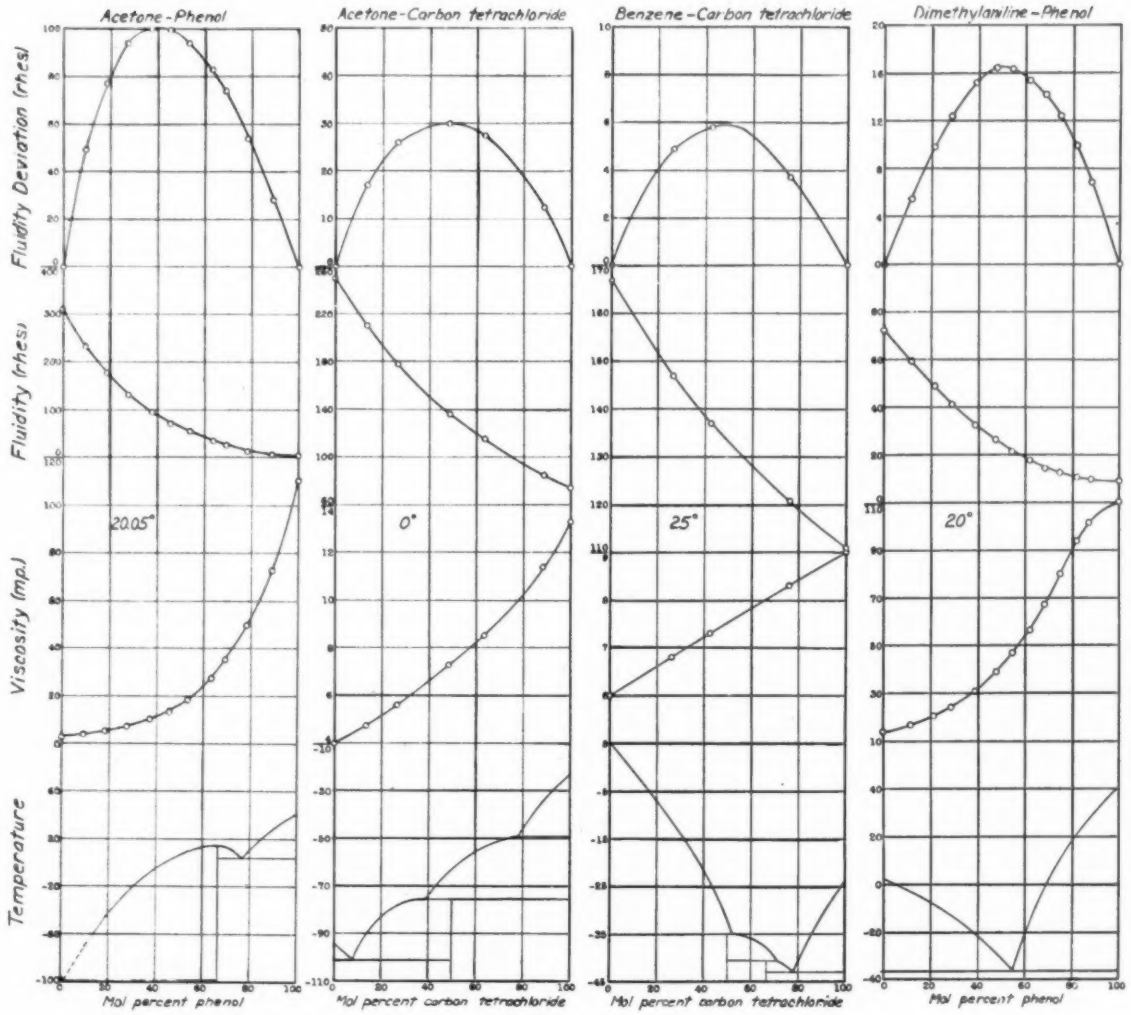

FIG. 11. FIG. 12. FIG. 13. FIG. 14.

0 and 10°, type I at 30, 40, 60, 80°, these irregularities disappear in the fluidity deviation curves. Kurnakov[7] had noticed in some mixtures that the maximum shifted towards the middle of the graph as the temperature was *lowered*, and so he made the generalization that the maximum did not coincide with the composition indicated by the freezing point curve, because the compound was partly dissociated in the liquid and that if the measurements could be made at a low enough temperature the maximum would occur at the expected composition. Bramley[7] made exactly the opposite observation on some other mixtures, namely, that the maximum shifted towards the middle of the graph as the temperature was *raised*, and he was led to the opposite generalization. Fig. 15 illustrates Bramley's data for the system pyridine-*o*-cresol. The maxima on the viscosity curves are quite definite when they are plotted on a larger scale and the exact positions of the maxima are indicated by the small arrows. It is seen that the fluidity deviation curves are all of the same form and have their maxima at the same composition, about 46 mole percent *o*-cresol.

As far as the writer is aware there is not a single example of a system which has a congruent or incongruent melting crystalline compound or compounds which does not give a negative fluidity deviation. There are a very few exceptions to the converse of this generalization

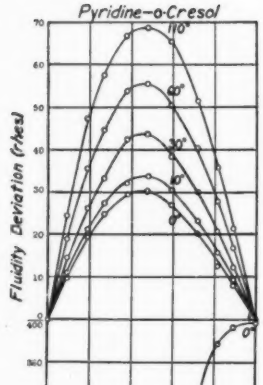

FIG. 15.

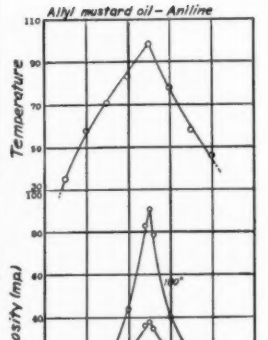

FIG. 16.

(omitting aqueous solutions which occupy a separate category), of which Fig. 14 illustrates one. It is very possible that the freezing point curve of this system does not represent true equilibrium, but is a metastable one. There are also a few exceptions to the rule that when the fluidity deviation is negative, the deviations in volume, heat content and vapor pressure are also negative. For example, the system benzene-carbon tetrachloride has a negative fluidity deviation and a small volume contraction, but a small heat absorption and a small positive vapor pressure deviation. However, Vold[6] has recently shown that the heat absorption in this system is much less than would be predicted by the theory assuming only van der Waals forces are active in the mixture.

A different type of viscosity-composition curve is that studied by Kurnakov for the two types of systems: stannic chloride with esters[7] and mustard oils with amines.[9] As shown in Fig. 16 the viscosity curves form sharp cusps at simple molecular ratios. The freezing point curve for allyl mustard oil and aniline (also shown in Fig. 16) comes to a sharp point at the 1 : 1 composition in contrast to the rounded maxima of the freezing point curves in Figs. 3–12. The freezing point curves of stannic chloride and some esters have been determined by Kurnakov,[7] and it is hard to tell from the data whether they form intersections or sharp maxima at the 1 : 2 composition.

This type of freezing point curve is evidently associated with a more definite type of combination than are the maxima with zero slope at the compound composition. Mustard oils and amines react with great violence and considerable evolution of heat to give substituted thioureas, so that a complete rearrangement and the formation of primary valence bonds has definitely occurred. The reaction between stannic chloride and esters is also quite violent, but nothing is known of the nature of the product. Similar viscosity and freezing point curves would be expected whenever an addition reaction involving the formation of primary valence bonds takes place, e.g., mixtures of ethylene and chlorine. Such systems are characterized by the compound having a much higher melting point and viscosity than either of the end components, and is really two separate systems in one.

DISCUSSION OF THE FLUIDITY DEVIATION CURVES

According to the view stated earlier, any interpretations of the curves of Figs. 3–15 in terms of compound formation in the liquid must come from the fluidity deviation curves. The systems of Figs. 3, 4, 7 and 12 all have 1 : 1 crystalline compounds and the maxima on the fluidity deviation curves also occur at or near the 1 : 1 composition in each case. This would appear to confirm the old assumption that some of the compound exists in the liquid phase and gives rise to the maximum deviation from the ideal at the composition where the concentration of the compound would be greatest according to the principles of homogeneous equilibrium, namely the 1 : 1 composition.

However, Figs. 7 and 11 illustrate systems where the single crystalline compound is not an equimolecular one, and Figs. 5, 6, 8, 10 and 13

[9] Kurnakov and Zemcuzny, Zeits. f. physik. Chemie **83**, 481 (1913); Kurnakov and Kwjat, ibid. **88**, 401 (1914).

where there are several crystalline compounds, and in all these the maximum in the fluidity deviation curve occurs at or near the 1 : 1 composition. The system acetone-phenol shows the greatest variation from the 1 : 1 composition with the maximum at about 40 mole percent phenol. Numerous other examples of these types could be cited confirming this observation.

These observations lead to the conclusion that there is no correlation between the position of the maximum fluidity deviation and the composition of the crystalline compounds indicated by the freezing point curve. The negative fluidity deviation, usually accompanied by volume contraction, evolution of heat and a negative vapor pressure deviation shows that the net attractive forces are greater in the mixture than in the pure components, and the symmetrical character of the fluidity deviation curves for all these different systems is significant. It indicates that *if* a compound is present in the liquid it is the equimolecular one regardless of what the crystalline compounds in the system may be.

This brings up a long moot question: Is there compound formation or not in the liquid? For example, is an equimolar mixture of acetone and chloroform at −90° composed of acetone molecules plus chloroform molecules plus a certain amount of acetone·chloroform molecules, or only molecules of the two end components? The former view has usually been tacitly assumed. In systems of the type shown in Fig. 16, compound formation involving primary valence bonds is quite definite, and the contrast between this behavior and that of the systems in Figs. 3–14 indicates that there is a difference of kind as well as of magnitude between the two types of systems.

If primary valence bonds are excluded, there remain hydrogen bonds, and dipole and van der Waals forces with which to explain the observed attractions. The negative deviations in the systems of Figs. 3, 5, 7, 8, 10, 11 and 14 can be explained by the formation of hydrogen bonds, oxygen or nitrogen donating electrons to hydroxyl or amino hydrogen. Glasstone[10] has discussed compound formation between tri- and tetrahalogenomethanes, and ethers and ketones. He concluded that there was a donation of electrons by ketone or ether oxygen to the hydrogen of chloroform or bromoform (which seems improbable, but possible), and to a chlorine of carbon tetrachloride (which seems still more improbable). However, there still remain the mixtures of benzene with carbon tetrachloride and with antimony trichloride, and a more reasonable view of all these mixtures where hydrogen bond formation is not a factor is a geometrical one according to which the molecules in the mixture are able to pack more closely giving a reduction in volume and an enhancement of the van der Waals attraction.

Irrespective of possible explanations, the lower fluidity definitely indicates a more orderly structure in the mixture than would be present in a completely random mixture of the pure components, and an arbitrary definition of compound formation in the liquid could be given in terms of the magnitude of the free energy difference between the partially ordered state and the completely random state as compared to kT.

The enhanced attractive forces which give rise to negative deviations from the ideal laws are apparently also responsible for the formation of crystalline compounds, but the composition of the compound (or compounds) in the crystal appears to be dictated chiefly by steric considerations. Pairs of substances with identical functional groups often form different compound, for instance, acetone forms 1 : 1 compounds with catechol and hydroquinol, but a 2 : 1 compound with resorcinol; and methyl oxalate forms a 1 : 4 compound with phenol, a 4 : 1 compound with hydroquinol, and no compounds at all with catechol, resorcinol or pyrogallol. When several compounds are formed in a system, e.g., ether-chloroform, the same attractive forces are probably responsible for all the compounds being formed, but several molecular ratios are evidently geometrically convenient in the crystal. The same question arises here as in the liquid: Is the crystal a molecular lattice of acetone·chloroform molecules, or a molecular lattice of acetone molecules and chloroform molecules in equimolecular proportions? Obviously, a knowledge of the crystal structure of some of these addition compounds would throw some light on the nature of the liquid.

I wish to thank Dr. Henry Eyring and Dr. Sterling B. Hendricks for reading the manuscript and for their suggestions.

[10] Trans. Faraday Soc. **32**, 200 (1936).

An Experimental Determination of Ultrasonic Velocity in Several Gases at Pressures Between One and One Hundred Atmospheres

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An acoustic interferometer of the resonator or driven type has been developed for the study of the behavior of ultrasonic waves in gases under pressures ranging from vacuum to several hundred atmospheres; measurements of acoustic velocity at several frequencies and in several gases at pressures ranging from one to 100 atmospheres have been made. Increase of velocity with pressure was found for air, N_2, He, and H_2, a decrease for CO_2, the approximate pressure and velocity ranges being respectively as follows: air, 1–101 atmos., 347–371 m/sec.; N_2, 1–102 atmos., 353–380 m/sec.; CO_2, 1–63 atmos., 270–198 m/sec. The He and H_2 were known to be impure. For them an increase in velocity nearly linear with pressure was found. Using frequencies from 88 to 499 kc dispersion was found for CO_2 at atmospheric pressure, but almost entirely disappeared above 8 atmospheres. The availability of this method for the indirect determination of specific heats is shown.

THE velocity of sound in gases has long been used in connection with other data for the evaluation of specific heats of gases.[1] Recently, through the work of Herzfeld and Rice, Kneser, Richards, and others on acoustic dispersion, and that of Grossmann, Knudsen, Kneser, Curtis and others[2] on acoustic absorption in gases and gas mixtures, these subjects have become of much wider interest. Thus far, because of difficulties inherent in most of the methods used, no attempt has been made to secure data at pressures far from atmospheric. At low frequencies, because of the relatively long wave-length, the apparatus is in general of large dimensions; at ultrasonic frequencies oscillators of the Pierce[3] type will not function at moderately high pressures. The resonator interferometer, developed for the study of gases in this laboratory,[4] is however well adapted to acoustic studies under high pressure conditions because the piezoelectric or magnetostrictive body used as the source may be driven by external means under any condition of pressure or temperature at which its respective electric or magnetic property is not suppressed. The author, in availing himself of this method, has developed an interferometer capable of withstanding pressures of more than 300 atmospheres, and presents herewith the results of measurements of acoustic velocity for several gases at pressures ranging from one to 100 atmospheres.

APPARATUS

The apparatus, the general plan of which is shown in Fig. 1, consists of a constant volume chamber in which is mounted a piezoelectric quartz disk having as electrodes a thin layer of gold sputtered on each of its plane faces, used as the source of plane waves, the disk diameter being large as compared to the wave-length to be measured; a plane plate reflector mounted on a nut movable by means of a micrometer screw, the control of which extended through a gas tight high pressure packing to the outside; a Bourdon type of pressure gauge; and a set of high pressure valves and fittings.

The chief features desired in this apparatus were: (1) a gas tight chamber which could be opened and resealed easily and as frequently as desired without tedious packing and sealing operations, (2) an external adjustment of the distance between the quartz plate and the movable reflector plate, (3) general adaptability to different problems and ease and rapidity of operation. The metal to metal gas tight seal and the high pressure packing through which the screw stem passed made possible this design. With the apparatus it was possible to make

[1] A. Eucken, *Handbuch der Exp. Phys.* Vol. 8, Part 1 (1929), p. 421.
[2] For extensive references, see D. G. Bourgin, Phys. Rev. **50**, 355 (1936).
[3] G. W. Pierce, Proc. Am. Acad. Arts and Sci. **60**, 271 (1925).
[4] J. C. Hubbard, Phys. Rev. **38**, 1011 (1931); **41**, 523 (1932); **46**, 525 (1934).

measurements to a high order of precision, yet it was of sufficient strength that once assembled and tightened up the matter of making measurements became practically a routine undertaking.

The chamber proper, the recess for the screw and nut, the screw thrust shoulder and mounting for the quartz plate were bored, at one lathe setting, out of a solid piece of cold rolled steel six inches in diameter. This was done on a precision lathe and very light finishing cuts were made to insure that all surfaces were true. The reflector plate was mounted on the end of a nut which moved in a hollow cylinder and had only a very small clearance between it and the cylinder wall. The small clearance kept the reflector plate approximately parallel to the quartz plate surface. Passages were provided to allow free passage of gas to all parts of the gas chamber.

The metal to metal seal which permitted the apparatus to be easily assembled and sealed was made by cutting a circular "v" shaped ring into a soft copper gasket with force sufficient to cause a slight flow of the copper metal. This method of sealing the chamber was very satisfactory. The cap was pulled down by 10 three-eighth inch cap screws. Making a perfectly tight gas seal at 100 atmospheres necessitated merely screwing these screws down with a wrench.

The seal at the packing was made by squeezing especially prepared soft leather washers against the screw stem and retainer wall. The stem of the screw had been hardened and ground sufficiently smooth so that there was a surprisingly small amount of friction between the packing and screw. The thrust due to the pressure in the chamber was carried by a ball thrust bearing, and the screw offered very little resistance to turning, it being easily possible to turn it with finger tip pressure under any conditions of pressure encountered in the range zero to 100 atmospheres. Any force arising from friction or pinching was not transmitted to the micrometer screw thread since it was inside the chamber and only subjected to the forces exerted by the weight of the moving nut.

A graduated head three inches in diameter which could be read directly to 0.005 mm was used to indicate fractions of revolutions, and a revolution counter served to indicate the position

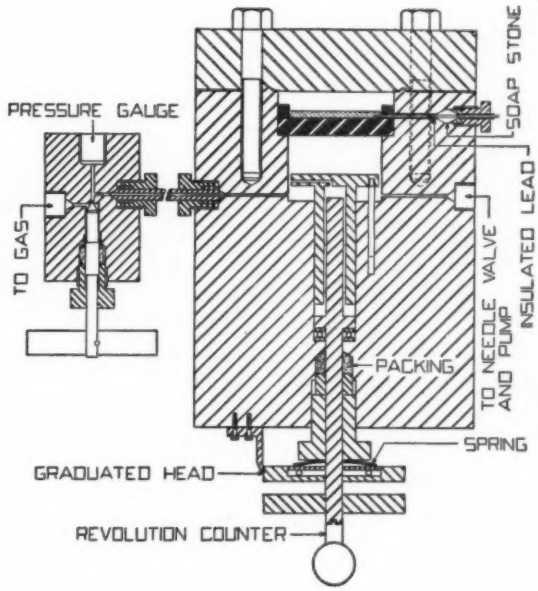

FIG. 1.

of the reflector plate in half-millimeters from the quartz plate surface.

DETERMINATION OF FREQUENCY

The driving frequency was generated by a precision Dow type oscillator which was loosely coupled to a two-stage resistance capacity coupled amplifier. Frequency measurements were made by carefully calibrating the precision oscillator by comparing its frequency by the heterodyne method with harmonics of several radio station frequencies. By using harmonics of the emitted carrier frequencies it was possible to get as many calibration points as were desired in any frequency range. Calibration curves were drawn on an open scale and any frequency was known to within one-tenth of a kilocycle per second. Since the natural frequency of vibration of the quartz plates varied with pressure it was necessary to measure the frequency at each pressure at which measurements were made.

MEASUREMENTS

Measurements were made of the velocity of ultrasonic waves in several gases and at pressure intervals of approximately 100 pounds per square inch from atmospheric pressure to 1500 pounds per square inch. Owing to the difficulty involved

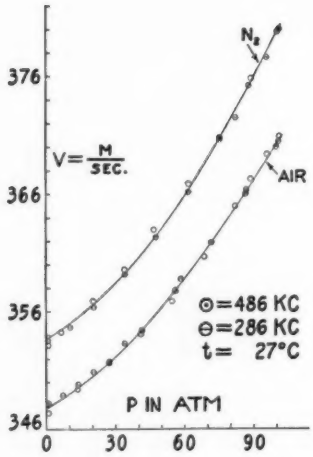

FIG. 2. Velocity of sound in air and in nitrogen as a function of pressure.

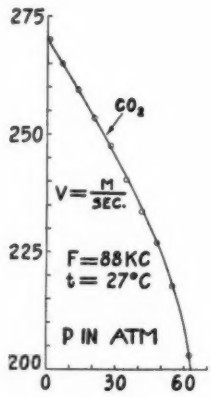

FIG. 3. Velocity of sound in carbon dioxide as a function of pressure.

in generating and compressing gases to the relatively high pressures used, gases which could be obtained commercially were studied. Gases which had been compressed over oil were used whenever possible, but no attempt was made to dry the gas or remove any impurities which the gas containers may have contained. However special precaution was taken to use only containers which were dry and to obtain the so-called "bone dry" gases.

Preparatory to making measurements, the laboratory was kept closed for a considerable period of time in order that it might come to as nearly as possible a constant temperature without using temperature control devices. The laboratory was one story below the ground level and showed variations of not more than 0.1 degree over a period of several hours. In addition, the acoustic chamber was wrapped with thick felt, and the power supplied the crystal was so small that in no case was there a detectable change of velocity with time. The apparatus was thoroughly flushed out with the gas to be used and was then exhausted with an oil pump before being filled with gas. The procedure used in making measurements consisted in filling the chamber to the highest pressure to be used, then waiting for the chamber to come to constant temperature and pressure, taking a set of six half wave-length readings at as near each end of the screw as absorption would permit, measuring the frequency and temperature, and proceeding to allow some of the gas to escape through a trap filled with oil until another desired pressure was reached, and then repeating the process.

A vacuum tube voltmeter was used to detect the nodes as the reflector plate was moved (always in the same direction) from the quartz plate. Only symmetrical crevasses which gave sharp responses were used, and a wall type galvanometer which was shunted by an arrangement which balanced out the steady component of the vacuum tube plate current was employed. The pitch of the lead screw was one-half millimeter and with the large calibrated head, it was possible to read the screw directly to 0.005 mm and to estimate to 0.001 mm.

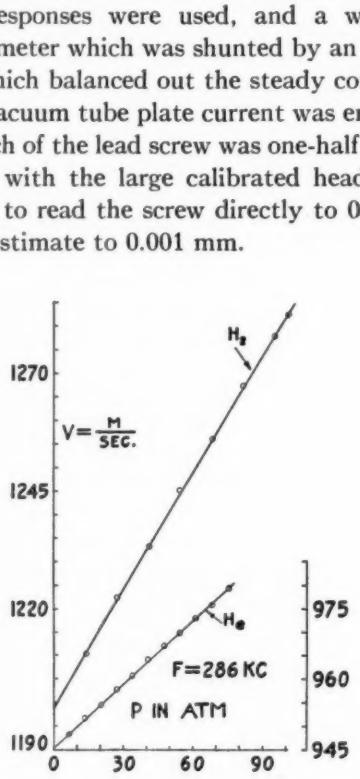

FIG. 4. Velocity of sound in hydrogen and in helium as a function of pressure.

Results

The variation of acoustic velocity with pressure in air, N_2, CO_2, and in He and H_2 known to contain impurities is shown in Figs. 2–4. The frequency given is in each case that of the crevasse at atmospheric pressure. As stated above, the response frequency of the quartz plate varied linearly with the pressure, a typical case being that of a plate having a response frequency of 188.6 kc at 1 atmos., and 190.0 kc at 69 atmos., a variation of 20.6 cycles or 0.011 percent per atmos. Except for CO_2 at the lowest pressures the velocities show no variation with frequency within experimental error. Air, N_2, and H_2 were studied at two frequencies, He at one, and CO_2 at six. Because of the absence of dispersion in any gas save CO_2, smooth curves are drawn through the assembled data for all the gases except CO_2. The temperature of each series was usually not more than one degree centigrade different from 27 degrees centigrade, the mean temperature of all the series. The results except for those of hydrogen which were reduced to 0 degrees centigrade have accordingly been reduced to that temperature.

The probable error of the measurements which were made in obtaining the following data is estimated to be approximately 0.2 percent, the major portion of this error arising from the pressure measurements. The deviation from the true velocities is not known since the exact amount of water vapor and other impurities in the gases is unknown; that this deviation is negligible is indicated by the values of γ, the ratio of specific heats, at atmospheric pressure, as shown in the succeeding paper.

Table I. *Ultrasonic velocity in air, N_2, He and CO_2 at 27°C and in H_2 at 0°C.*

p (atm)	Air	N_2	He	H_2	CO_2
0	[347.8]	[353.3]			[270.8]
1	347.9	353.4	945.7	1199.5	270.1
10	349.0	354.6	949.8	1207.2	262.2
20	350.5	356.4	954.2	1215.7	254.0
30	352.2	358.3	958.8	1224.2	245.2
40	354.2	360.6	963.3	1232.3	234.6
50	356.4	363.2	968.0	1240.6	223.2
60	358.8	366.0	972.4	1249.0	208.8
70	361.5	369.0	977.0	1257.3	
80	364.4	371.9		1265.4	
90	367.3	375.8		1273.4	
100	370.3	379.4		1281.4	

Table II. *Dispersion of CO_2 as a function of pressure. $t=27$ deg. C.*

P (atm)	V. at 88.4 kc	97.8 kc	188.7 kc	209.9 kc	284.6 kc	498.7 kc
1	270.1		270.7	272.0	272.9	273.5
10	262.2	262.5	262.7	262.1	263.6	263.2
20	254.0	254.2	253.6	253.5	254.8	254.1
30	245.2	245.1	243.9	244.5	245.2	244.7
40	234.6	234.6	233.3	234.6	235.0	234.5
50	223.2	221.2	220.7	222.9	222.7	222.9
60	208.8	203.0	200.5	205.6	205.8	207.5

Table I shows the results read from smoothed curves for air and N_2 at 286 and 486 kc, for CO_2 at 88.39 and for He and H_2 at 286 kc. Table II shows the results for CO_2 at six frequencies. As expected[5] evidence of molecular dispersion largely disappears at moderately low pressures in the frequency range studied.

The velocities for hydrogen and for helium were low owing to impurities, the variations of velocity with pressure being linear in helium and very nearly so in hydrogen and in good proportionate agreement with results computed from thermodynamic data.

An incidental result of interest is the effect of pressure on response frequency and crevasse characteristics of the quartz plates used as the source. Modern precision methods of measurement of frequency variation suggest the possibility of developing piezoelectric pressure gauges of far greater sensitivity than are at present available; the added features of continuous reading and remote control should find many obvious uses for them.

The author wishes to express his thanks to Professor J. C. Hubbard under whose direction this work was done.

[5] W. T. Richards and J. A. Reid, J. Chem. Phys. **2**, 193 (1934).

Ratio of Specific Heats of Air, N_2, and CO_2 as a Function of Pressure by the Ultrasonic Method

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Measurements have been made by Hodge of ultrasonic velocities at 27°C at pressures from 1 to 100 atmos. in air and N_2 and at 1 to 60 atmos. in CO_2. The results for air and N_2 combined with the respective compressibility data of Holborn and Otto give at 27°C for air, values of γ between 1.406 at 1 atmos. and 1.580 at 100 atmos., and for N_2, 1.403 at 1 atmos. to 1.564 at 100 atmos. The acoustic velocities in CO_2 combined with the compressibility data of Amagat, give for γ at 27°C values from 1.304 at 1 atmos. to 3.524 at 60 atmos. These and the other results between these limits are in excellent general agreement with the few results in this temperature and pressure region available for comparison.

AMONG the indirect methods for the evaluation of C_v, the specific heat at constant volume, or of γ, the ratio of specific heats, the acoustic method is the simplest and most convenient, and has accordingly been the subject of numerous and painstaking researches.[1] These studies have largely been confined to audible frequencies and have yielded only meager results, subject in most cases to very large errors. The determination of acoustic velocities at audible frequencies requires either the use of such large scale apparatus as to restrict the method to the commonest gases, or, if done by the more usual methods of resonators or of the Kundt's tube, correction factors are necessary. The determinations of the corrections have entailed a great deal of theoretical and empirical work and the results have been satisfactory in but few cases. An additional difficulty, only lately recognized, is the possibility of acoustic dispersion of the molecular type, in some cases amplified by traces of gaseous impurity.

The experimental resources which have lately become available through the development of ultrasonic methods of measuring acoustic velocity permit the use of small scale apparatus which at the same time is large enough in terms of wavelengths to reduce to a negligible amount the corrections made necessary by diffraction and the departure from the adiabatic condition encountered when a sound wave is confined to a tube of a diameter small compared to wavelength. By a suitable choice of pressure and frequency the experiments can be carried out so as to explore the effects of dispersion of the molecular type.[2]

The ratio of specific heats, γ, may be found from the value of acoustic velocity, V, and the equation of state. Thus

$$V^2=(\partial p/\partial \rho)_s=-v^2\gamma(\partial p/\partial v)_T.$$

Since the equation of state is seldom known over more than a very narrow range of variables, a more direct course consists in using the isothermal values of pv. Thus, putting $(pv)_T=f(p)$, we have

$$\gamma=\frac{pv-p[\partial(pv)/\partial p]_T}{(pv)^2}V^2.$$

In the following a computation of γ has been made using Hodge's data for V, given in the preceding paper, and the compressibility data of Holborn and Otto[3] for air and for N_2 and the compressibility data of Amagat[4] for CO_2.

The compressibility data $(pv)_T=f(p)$, allow of interpolation to 27°C in the pressure ranges noted below. The interpolations were made algebraically, terms including the second order being usually sufficient. The interpolation equations were tested by extrapolation from them to temperatures not used in setting them up. From the curves $(pv)_{27}=f(p)$, thus obtained, values of pv and of $d(pv)/dp$ were taken at

[1] For a summary, see Eucken, *Handbuch der Exp. Phys.* Vol. 8, Part 1 (1929), pp. 424–425.

[2] Richards and Reid, J. Chem. Phys. **2**, 193 (1934).
[3] Holborn and Otto, Zeits. f. Physik **33**, 1 (1925).
[4] Amagat, Comptes rendus **118**, 450 (1891).

various pressures as desired. A large scale plot was made in the case of each gas of the values of acoustic velocity *vs.* pressure (p, V), and the best curves found by graphical methods. Values of V for use in the computations were then taken from the curves at desired pressure intervals.

Air

The curve (p, V) was obtained by using Hodge's acoustic measurements at both 286 and 486 kc, since no dispersion is evident in the results. Computations of γ were made for pressures of 0, 1, and at intervals of 10 up to 80 m Hg. The results are shown in Fig. 1, pressures being given in atmos. For comparison, the following results are available by interpolation to 27°C from the work of Jacob,[5] determined from thermodynamic data.

p. kg/cm²	(Jacob)	(H and H)
0	1.400	1.404
50	1.485	1.491
100	1.562	1.574

Nitrogen

The results, similarly found, are shown in Fig. 1. No values have been found for comparison.

CO_2

The compressibility data of Amagat allow of the interpolation of $(pv)_T = f(p)$ to 27°C between 35 and 60 atmos. Hodge's acoustic data for CO_2 at 88 kc, where dispersion was least evident at atmospheric pressure, were chosen for computations. The results for γ are shown in Fig. 1. For comparison the following values have been

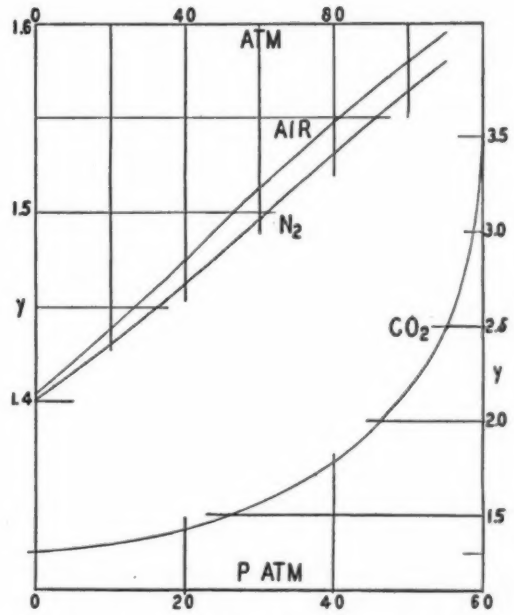

FIG. 1. Ratio of specific heats of air, N_2 and CO_2 at 27°C as a function of pressure.

computed from the results of Worthing.[6]

p. atmos.	(Worthing)	(H and H)
0	——	1.304
10	1.33	——
20	1.41	——
30	1.55	1.560
40	1.77	1.780
50	2.10	2.167
60	——	3.524

The results of this study show the feasibility of greatly extending, by relatively simple experimental means, the knowledge of γ and of C_v over the broad temperature and pressure ranges for which excellent data for $(pv)_T = f(p)$ are available for several gases. The precision measure of γ in the present results is, at atmospheric pressure, 2/10 percent, at other pressures, 4/10 percent.

[5] M. Jacob, Zeits. f. tech. Physik **4**, 460 (1923).

[6] A. G. Worthing, Phys. Rev. **32**, 244 (1911); **33**, 217 (1911).

Rotatory Dispersion of Configurationally Related Unsaturated Secondary Carbinols and Their Corresponding Chlorides

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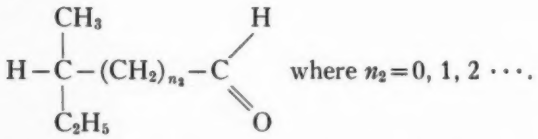
In several instances a periodic change in sign of the partial rotation of the chromophoric groups has been observed with the increase in the distance of these groups from the asymmetric carbon atom. In many unsaturated substances, the ethylenic bond is known to possess a partial rotation of significant value. It was desired to determine whether this partial rotation is subject to a periodic change in sign with the progressive increase in the distance of the double bond from the asymmetric center. The observations reported here seem to indicate that such a change exists although it is expressed less strikingly than in the case of the carbonyl group previously discussed.

WORK previously reported from this laboratory[1] has brought out the fact that in configurationally related substances the partial rotation of a definite absorption band of a functional group (or of a group with distinct chromophoric properties), may change its sign with the change in the distance of the group from the asymmetric center by one $-CH_2$ radical. The most striking illustration of this phenomenon is presented in the series of configurationally-related aldehydes of the general type



where $n_2=0, 1, 2 \cdots$.

TABLE I. *Maximum rotations* $[M]^{25}_{5780}$ *of unsaturated and saturated configurationally related substances in homogeneous state.*

CH_2=CH	CH_2=CH	CH_3 CH_2=CH	CH_2=CH CH_2
H...C...OH	H...C...OH	H...C...OH	H...C...OH
C_4H_9	C_5H_{11}	CH_3	CH_3
−28.1°	−33.3°	−0.35°	−4.9°
Chloride = −18°	Chloride = −34°	Chloride = −13°	Chloride = −20°
C_2H_5	C_2H_5	C_3H_7	C_3H_7
H...C...OH	H...C...OH	H...C...OH	H...C...OH
C_4H_9	C_5H_{11}	CH_3	CH_3
+9.8°	+11.1°	−12.5°	−12.5°

[1] P. A. Levene and A. Rothen, J. Chem. Phys. **4**, 48 (1936).

In this group of substances, the absorption band at λ2950 is strongly anisotropic, but the circular dichroism is of opposite sign in the first two members of the series homologous with respect to n_2 ($n_2=0$ and $n_2=1$).

Aliphatic unsaturated carbinols with one double bond represent a series in a sense similar to that of the aldehydes, inasmuch as the group with the ethylenic linkage has a distinct absorption band absent in each of the remaining three substituents on the asymmetric carbon atom. Hence it was desired to ascertain whether the effect of distance of the ethylenic bond from the

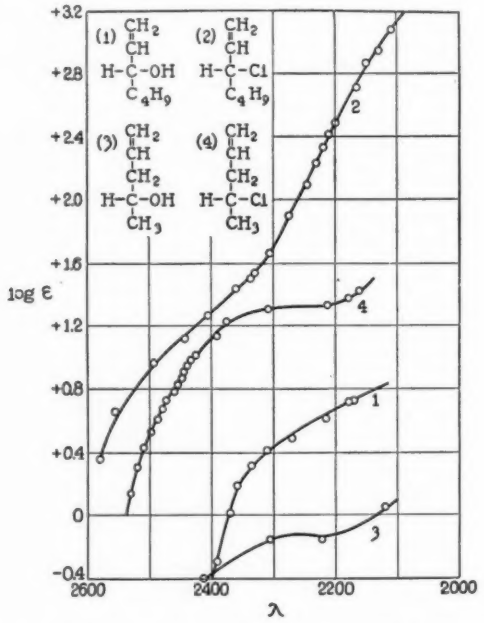


FIG. 1. Absorption curves of some unsaturated substances.

TABLE II. *Rotatory dispersion of levo-1-hepten-3-ol (vinylbutyl carbinol) and the corresponding levo-3-chloroheptene-1 and levo-3-bromoheptene-1 in homogeneous state.*

CARBINOL			CHLORIDE			BROMIDE	
Constants of sample: $d_4^{20}=0.8315$, $d_4^{25}=0.8356$ (in vacuum), $n_D^{25}=1.4313$ Visible region: $l=20$ cm U.V. region: $l=5$ cm from λ3840 to λ2599, 0.1 cm from λ2440 to λ2384, 0.05 cm for λ2340 $[M]^{25}_{max}=-\frac{23.2830}{\lambda^2-0.0365}+\frac{15.7476}{\lambda^2-0.020}$			Constants of sample: $d_4^{25}=0.8883$ (in vacuum), $n_D^{25}=1.4380$ Visigle region: $l=20$ cm U.V. region: $l=5$ cm from λ3830 to λ2960, 1 cm from λ2920 to λ2775, 0.1 cm for λ2600 $[M]^{25}_{max}=-\frac{49.5878}{\lambda^2-0.0365}+\frac{45.4628}{\lambda^2-0.029}$			Constants of sample: $d_4^{25}=1.1640$, $n_D^{25}=1.4697$ Visible region: $l=10$ cm U.V. region: $l=1$ cm $\alpha=-\frac{29.976}{\lambda^2-0.041}+\frac{26.986}{\lambda^2-0.030}$	
λ	α^{25}	$[M]^{25}_{max}$	λ	α^{25}	$[M]^{25}_{max}$	λ	α^{25}
6678.1	−28.78	-19.87_6	5875.6	−14.636	−12.700	5780.1	−13.552
5875.6	−39.095	−27.000	5780.1	−15.286	−17.616	5460.7	−15.927
5780.1	−40.688	−28.100	5460.7	−17.875	−20.600	4358.3	−32.53
5460.7	−46.860	−32.363	4358.3	−35.305	−40.687	4046.6	−42.42
4358.3	−85.63	−59.069	4046.6	−45.39	−52.31	3910	−4.90
4046.6	−106.29	−73.406	3830	−13.9	−64.1	3810	−5.40
3840	−31.13	−86.00	3635	−16.9	−77.9	3740	−5.90
3668	−36.14	−99.84	3528	−18.9	−87.1	3665	−6.40
3525	−41.14	−113.6	3450	−20.9	−63.4	3595	−6.90
3414	−46.15	−127.5	3405	−21.9	−100.9	3490	−7.90
3320	−51.15	−141.3	3340	−23.9	−110.1	3200	−1.20 (1 mm)
3240	−56.15	−155.1	3310	−24.9	−114.8	3100	−1.40 (1 mm)
3108	−66.17	−182.8	3250	−26.9	−124.0		
2998	−76.18	−210.4	3200	−28.9	−133.2		
2915	−86.19	−238.1	3177	−29.9	−137.8		
2844	−96.20	−265.7	3135	−31.9	−147.0		
2785	−106.2	−293.4	3090	−33.9	−156.3		
2735	−116.2	−321.0	3075	−34.9	−160.9		
2690	−126.2	−348.6	3040	−36.9	−170.1		
2650	−136.2	−376.2	3010	−38.9	−179.3		
2615	−146.2	−403.9	2960	−41.9	−193.1		
2599	-151.2_5	−417.8	2920	−9.0	−207		
2440	-4.5_0	$-62._2$	2890	−9.5	−219		
2420	-4.7_5	$-65._6$	2867	−10.0	−230		
2400	-5.0_0	$-69._1$	2840	−10.5	−242		
2384	-5.2_5	$-72._5$	2775	−12.0	−276		
2340	-2.9_0	$-80._1$	2600	−1.8	−415		

asymmetric center would be analogous to the phenomena observed in the series of aldehydes.

The rotatory dispersions of the configurationally related substances given in Table I were determined. For reasons discussed in another article,[2] identical direction of rotation was assigned to configurationally related secondary carbinols and halides.

For the sake of convenience the corresponding saturated carbinols have been included in Table I.

ABSORPTION SPECTRA

It is known that the first intense absorption region of an aliphatic unsaturated hydrocarbon with only one double bond is located at about λ1900−λ1850.[3] Fig. 1 represents the absorption curves of two carbinols and of their corresponding chlorides. Inspection of the curves brings out two facts: First, the substitution of the chlorine atom for the hydroxyl group enhances considerably the absorption of the unsaturated compound; second, the nearer the distance between the double bond and the functional group (hydroxyl group or chlorine atom), the stronger the absorption. These results were to be expected from the knowledge of absorption spectra of organic molecules.

ROTATORY DISPERSION

The rotatory dispersion measurements are summarized in Tables II to V.

[2] P. A. Levene and A. Rothen, J. Biol. Chem. **121**, 747 (1937).

[3] C. P. Snow and C. B. Allsopp, Trans. Faraday Soc. **30**, 93 (1934).

TABLE III. *Rotatory dispersion of levo-1-octene-3-ol (vinyl-amyl carbinol) and the corresponding chloride, levo 3-chloro-octene-1, in heptane solution.*

CARBINOL			CHLORIDE		
Constants of sample: $d_4^{25}=0.8324$ (in vacuum), $n_D^{25}=1.4346$			Concentration = 0.777 M, $l=10$ cm, 1 cm for λ2600 and λ2575, 0.1 cm for λ2370		
Concentration = 1.0167 M					
Visible region: $l=40$ cm					
U.V. region: $l=10$ cm from λ3685 to λ2650, 1 cm from λ2560 to λ2350, 0.1 cm for λ2200					
$[M]^{25}_{max}=-\frac{32.496}{\lambda^2-0.0365}+\frac{23.669}{\lambda^2-0.022}$			$[M]^{25}_{max}=-\frac{65.32}{\lambda^2-0.037}+\frac{60.22}{\lambda^2-0.010}$		
λ	α^{25}	$[M]^{25}_{max}$	λ	α^{25}	$[M]^{25}_{max}$
6678.1	−6.575	−23.50	4000	−1.90	−127
5875.6	−8.952	−31.994	3800	−2.40	−160
5780.1	−9.333	−33.356	3640	−2.90	−193
5460.7	−10.761	−38.460	3510	−3.40	−227
4358.3	−19.82	−70.84	3410	−3.90	−260
3685	−6.9	−118	3315	−4.40	−293
3420	−8.9	−152	3245	−4.90	−327
3170	−11.9	−204	3170	−5.40	−360
2951	−15.9	−272	3120	−5.90	−393
2850	−18.9	−323	3020	−6.90	−460
2770	−21.9	−375	2960	−7.40	−493
2650	−27.9	−477	2930	−7.90	−527
2560	−3.5	−600	2875	−8.90	−593
2540	−3.7	−630	2820	−9.90	−660
2460	−4.5	−770	2780	−10.90	−727
2438	−4.8	−820	2600	−1.50	−1000
2417	−5.1	−870	2575	−1.60	−1070
2390	−5.6	−960	2370	−0.30	−2000
2373	−5.9	−1010			
2350	−6.2	−1060			
2200	-1.1_5	−1970			

TABLE IV. *Rotatory dispersion of levo-1-penten-4-ol (methyl-allyl carbinol) and the corresponding chloride in homogeneous state.*

CARBINOL			CHLORIDE		
Constants of sample: $d_4^{25}=0.8327$ (in vacuum) $n_D^{25}=1.4220$			Constants of sample: $d_4^{25}=0.8794$ (in vacuum) $n_D^{25}=1.4218$		
Visible region: $l=10$ cm			Visible region: $l=10$ cm		
U.V. region: $l=5$ cm, 1 cm for λ3060			U.V. region: $l=5$ cm, 1 cm from λ2715 to λ2640		
$[M]^{25}_{max}=-\frac{1.4070}{\lambda^2-0.046}$			$[M]^{25}_{max}=-\frac{15.474}{\lambda^2-0.026}+\frac{9.6138}{\lambda^2-0.013}$		
λ	α^{25}	$[M]^{25}_{max}$	λ	α^{25}	$[M]^{25}_{max}$
5875.6	−1.415	−4.700	5875.6	−5.100	−19.50
5780.1	−1.469	−4.879	5780.1	−5.305	−20.28
5460.7	−1.682	−5.587	5460.7	−6.049	−23.12
4358.3	−2.95	−9.80	4358.3	-10.47_5	−40.05
4046.6	−3.57	−11.86	4046.6	−12.70	−48.56
3855	−2.10	−13.9	3875	−7.10	−54.3
3715	−2.35	−15.6	3700	−8.10	−61.9
3585	−2.60	−17.3	3550	−9.10	−69.6
3475	−2.85	−18.9	3420	−10.10	−77.2
3370	−3.10	−20.6	3312	−11.10	−84.9
3300	−3.35	−22.2	3220	−12.10	−92.5
3060	−0.90	−30	3143	−13.10	−100.2
			3070	−14.10	−107.8
			3013	−15.10	−115.5
			2900	−17.10	−130.8
			2860	−18.10	−138.4
			2810	−19.10	−146.0
			2778	−20.10	−153.7
			2755	−20.60	−157.5
			2715	−4.35	−166
			2670	−4.60	−176
			2640	−4.85	−185

SUBSTANCES WITH THE ETHYLENIC GROUP ATTACHED TO THE ASYMMETRIC CARBON ATOM

From the tables it can be noticed first that the rotation of 2-penten-4-ol is opposite in sign in homogeneous state and in ether solution. Many other similar cases are known.[4] It has been pointed out in other articles that this phenomenon occurs only when the two principal partial rotations are of opposite sign. In one state the first partial rotation has a higher numerical value, whereas in the other it has a lower value than the other partial rotation. In one state the rotatory dispersion is anomalous. The rotatory dispersion of 2-penten-4-ol proved anomalous in ether solution.[5]

As seen from Tables II, III and V, *the vinyl and crotonyl derivatives (carbinols and chlorides)* are extremely dispersive and from that point of view they differ widely from the corresponding saturated substances. This great increase in the dispersive power results from the two following causes. First, the first optically active band is located nearer in the U.V. region. Second, the two principal partial rotations are of opposite sign and not much different in magnitude.

The rotatory dispersion of a few carbinols belonging to the vinyl series (methyl-, ethyl-, propyl- and butylvinylcarbinols) have already been investigated in the visible region by Kenyon and Snellgrove.[6] These authors came to

[4] P. A. Levene and A. Rothen, J. Biol. Chem. **116**, 209 (1936).

[5] We wish to correct an error which appeared in previous papers on unsaturated derivatives [J. Biol. Chem. **83**, 579 (1929); J. Org. Chem. **1**, 76 (1936)]. The fact that the rotation of 2-penten-4-ol can be of either sign, according as the measurements are taken in ether or in homogeneous state, had been overlooked and the wrong sign of rotation was attributed to this compound for comparison with other related unsaturated carbinols.

[6] J. Kenyon and D. R. Snellgrove, J. Chem. Soc. **127**, 1169 (1925).

TABLE V. *Rotatory dispersion of 2-penten-4-ol (methylcrotonyl carbinol) and the corresponding chloride.*

CARBINOL					CHLORIDE		
in Homogeneous State			in Ether Solution		in Homogeneous State		
Constants of sample: $d_4^{25}=0.8305$ (in vacuum), $n_D^{25}=1.4264$ Visible region: $l=20$ cm U.V. region: $l=5$ cm $[M]^{25}_{max}=-\frac{6.558}{\lambda^2-0.0365}+\frac{6.767}{\lambda^2-0.022}$			Concentration $=1.098\ M$, $l=40$ cm $[M]^{25}_{max}=-\frac{5.593}{\lambda^2-0.0365}+\frac{8.261}{\lambda^2-0.022}$		Constants of sample: $d_4^{25}=0.885_5$ (in vacuum), $n_D^{25}=1.4310$ Visible region: $l=10$ cm U.V. region: $l=5$ cm 1 cm from λ3080 to λ2820 $[M]^{25}_{max}=-\frac{27.03}{\lambda^2-0.0365}+\frac{23.57}{\lambda^2-0.029}$		
λ	α^{25}	$[M]^{25}_{max}$	α^{25}	$[M]^{25}_{max}$	λ	α^{25}	$[M]^{25}_{max}$
5875.6	−0.202	−0.303	+1.163	$+7.67_5$	5780.1	−1.147	−13.55
5780.1	−0.236	−0.354	+1.291	+8.52	5460.7	−1.333	−15.75
5460.7	−0.373	−0.559	+1.93	+12.7	4358.3	−2.53	−29.9
4358.3	−1.63	−2.44	+2.13	+14.3	4046.6	−3.17	−37.5
4046.6	−2.53	−3.80			3750	−2.05	−48.4
3750	−1.00	−6.00			3535	−2.55	−60.2
3600	−1.25	−7.50			3450	−2.80	−66.1
3500	−1.50	−9.00			3380	−3.05	−72.1
					3080	−0.87	−103
3400	−1.75	−10.5			3020	−0.97	−114
3320	−2.00	−12.0			2960	−1.07	−126
3275	−2.25	−13.5			2920	−1.17	−138
3230	−2.50	−15.0			2820	−1.37	−162
3170	−2.75	−16.5					
3140	−3.00	−18.0					

the conclusion that the dispersion of such compounds could be represented by a single Drude term, the λ_0^2 values increasing slightly in the series from 0.0528 for the methyl derivative to 0.0582 for the butyl derivative. Our more accurate measurements, however, show that there is a discrepancy amounting to $\backsimeq$0.6 percent for the visible range between experimental values and those calculated from a single Drude term. In the U.V. region the discrepancies increase and the course of dispersion deviates strongly from that required by a single term. Analysis shows that the rotatory dispersion is fairly well expressed by two terms opposite in sign, the dispersion constant of the first term being $\lambda_1^2=0.0365$.

The fact that the same value has been found for the chlorides permits the conclusion that for the chlorides as well as for the carbinols the first major contribution is located in the double bond. These results show that the absorption region λ2400−λ2000 (which is a region of weak absorption for the vinyl carbinols but of strong absorption for the vinyl chlorides) does not furnish an appreciable rotatory contribution contrary to the expectation based on rotatory dispersion measurements of small accuracy limited to the visible range. The dispersion constants $\lambda_0^2=0.0528$ to $\lambda_0^2=0.0582$ have no physical significance.

Attention is called to the fact that vinylamyl carbinol and crotonylmethyl carbinol have the same sign of rotation when the two corresponding saturated carbinols obtained from them by hydrogenation rotate in opposite directions. This phenomenon may be explained by the following considerations. In secondary saturated carbinols the rotation is determined by the clockwise or counterclockwise arrangement of the groups $R_1-\underset{\displaystyle H}{\overset{\displaystyle |}{\underset{|}{C}}}-R_3$ according to their volume. The sign of rotation is the same in all members having $R_1<R_3$; the sign is opposite in members having $R_3<R_1$. In the vinyl or crotonyl derivatives, the major partial rotation is furnished by the ethylenic group. The sign of this partial rotation is determined by clockwise or counter-

clockwise arrangement (by volume) of the groups $H-\overset{|}{\underset{|}{C}}-OH$ (R). The arrangement does not change with the change of R from a group of a smaller to that of a higher volume since when $R=CH_3$, the volume of the methyl group is already larger than that of the remaining two groups.

Effect of the Increase in Distance of the Ethylenic Group from the Asymmetric Center

In this connection 1-penten-4-ol will be discussed. The rotatory measurements are summarized in Table IV. It may be seen that in this case carbinol and halide are considerably less dispersive than the corresponding vinyl or crotonyl derivatives. The small rotation of the alkyl carbinol did not permit the resolution of the dispersion curve into two terms, but the analysis of the dispersion of the chloride shows that the origin of the first rotatory contribution is located further in the ultraviolet region ($\lambda_1^2=0.026$) than the first partial rotation of the vinyl derivatives. In fact the value of the dispersion constant of the first contribution of this substance is nearly the same as that of the *second* partial contribution of the vinyl or crotonyl series. Hence for the chlorides it might be assumed that corresponding bands in members of the two series—alkyl and vinyl or crotonyl series—are of opposite sign. On the other hand, the absorption region corresponding to $\lambda_1^2=0.036$ furnishes an insignificant contribution in methylalkyl carbinol. Thus the effect of the distance from the asymmetric center of the significant chromophoric group is not brought out clearly in the case of ethylenic derivatives. Nevertheless the value of the first dispersion constant of alkylmethyl carbinol seems to indicate that the effect of distance exists also in the ethylenic series. It is not impossible that in the higher homologues of the alkyl series the effect of distance will come more clearly to the front.

Experimental

Compounds

The compounds were carefully fractionated and titration of the double bond by bromine was carried out for each of them.

The maximum molecular rotations have been calculated from the accepted maximum values for the saturated carbinols and from the values of the rotations of the saturated carbinols obtained by reduction of the unsaturated ones. The degree of racemization occurring in the preparation of the chlorides from the carbinols being unknown, the maximum values given for the former are only minimum values. They are "least maximum values."

The rotatory measurements were carried out as previously described. The same precautions were taken and the same precision is claimed.

The agreement between observed and calculated values from a two term formula is satisfactory.

For vinylbutyl carbinol, the deviations between experimental and calculated rotations are within experimental error over the visible range of the spectrum (<0.05 percent). In the U.V. range, deviations >0.5 percent do not occur.

For vinylamyl carbinol, the deviations are greater, 0.1 percent in the visible range and from 1 to 5 percent in the U.V. range. The deviations are systematic and would probably be reduced by splitting the second term into two terms of opposite sign. The small angles of rotation observed did not seem to warrant this calculation.

For 3-chloroheptene-1 the deviations observed are 0.05 percent in the visible range and 0.5 percent in the U.V. region. Discrepancies of the order of 1 percent are observed for 3-chlorooctene-1, no rotation being measured in the visible range of the spectrum.

Rotatory Dispersion of Configurationally Related Alkyl Azides

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From the viewpoint of chemical behavior, the $-N_3$ group may be regarded as a pseudohalogen. Like iodides, azides possess an absorption band in the near ultraviolet region. For both practical and theoretical reasons it was important to obtain information on the rotatory properties of the azides as compared with those of the corresponding halides. The correlation of the configurations of primary and secondary azides is discussed in this communication. From the analysis of the rotatory dispersion of the primary azides and halides it became evident that the partial rotations of the azido group and of the halogen atom may be of opposite sign in configurationally related substances. An unexpected observation was made with regard to the members of a homologous series of secondary azides, namely, the rotation in the visible region as well as the partial rotation of the azido group, changes sign on passing from the second member of the series to the third. A tentative explanation of the phenomenon is given. It was found that in all alkyl azides the absorption band at λ2880 is not anisotropic or at best, insignificantly so.

THE rotatory dispersions of azides of the general type

$$\begin{array}{l} (CH_2)_{n_1}CH_3 \\ | \\ H-C-(CH_2)_{n_2}N_3 \\ | \\ (CH_2)_{n_3}CH_3 \end{array}$$

are presented in this communication.

The azido group possesses chemical properties analogous to those of the halogen atoms. Similarly to iodides, azides possess an absorption band in the near ultraviolet region. The azides can be converted into the corresponding amines without change of configuration.[1] The configurations of the primary and secondary amines were correlated with a sufficient degree of certainty. Thus it may be accepted that the configuration of primary and secondary azides are likewise correlated. With this knowledge it is now possible to investigate the effect of the value of n_2 on the partial rotation of the N_3 group and furthermore to test the applicability of this information to the correlation of the configurations of primary and secondary halides.

At the outset it may be stated that in homologous series of primary and of secondary azides, a phenomenon was encountered which does not occur in the corresponding halides. In azides having $n_2=0$ the rotation of the higher members of the series homologous with respect to n_1 are of opposite sign from those of the lower members. In the azides having $n_2=1$ the same phenomenon is observed in the series homologous with respect to n_3. In the halides, however, the rotations remain of the same sign all through the series. To find an explanation of this phenomenon, a knowledge of the rotatory dispersion of the azides was required.

All data concerning the dispersions can be seen in Tables I to III. The values found in the

TABLE I. *Rotatory dispersion of configurationally related secondary azides in heptane.*

	DEXTRO 2-AZIDOBUTANE $d_4^{25}=0.8619$ (in vacuum) $n_D^{25}=1.4122$ Conc. 1.673 *M* Visible region: *l* = 40 cm U.V. region: *l* = 10 cm 0.1 cm for λ2450 $[M]^{25}_{calc}=\frac{12.712}{\lambda^2-0.0296}$		DEXTRO 2-AZIDOOCTANE $d_4^{25}=0.8555$ (in vacuum) $n_D^{25}=1.4332$ Conc. 0.645 *M* Visible region: *l* = 40 cm U.V. region: *l* = 5 cm 0.5 cm from λ3370 to λ2450 $[M]^{25}_{calc}=\frac{15.970}{\lambda^2-0.0309}$	
λ	α^{25}	$[M]^{25}$	α^{25}	$[M]^{25}$
5892.6	—	—	10.718	50.49
5875.6	11.938	40.22	—	—
5780.1	12.379	41.71	11.171	52.68
5460.7	14.048	47.33	12.681	59.74
4358.3	23.53	79.27	21.31	100.39
4046.6	28.04	94.47	25.47	120.00
3830	7.90	106.5	—	—
3760	8.40	113.2	—	—
3750	—	—	3.82	144
3720	8.50	114.5	—	—
3585			4.32	163
3370			0.52	196
3220			0.62	234
3020			0.35 (conc. 0.322 *M*)	264
2800			0.38 (conc. 0.258 *M*)	360
2450	0.35	470	0.60 (conc. 0.258 *M*)	570

[1] P. A. Levene and A. Rothen, J. Biol. Chem. **115**, 415 (1936).

TABLE II. *Rotatory dispersion of configurationally related secondary azides.*

	DEXTRO 3-AZIDOHEPTANE $d_4^{25}=0.8583_5$ (in vacuum) $n_D^{25}=1.4298$		DEXTRO 3-AZIDONONANE $d_4^{25}=0.8575$ (in vacuum) $n_D^{25}=1.4373$		LEVO 4-AZIDOOCTANE $d_4^{25}=0.8591$ (in vacuum) $n_D^{25}=1.4337$			
					in heptane		homogeneous state	
	Conc. 0.854 *M* (in heptane) $l=100$ cm $[M]^{25}_{calc}=\frac{1.2413}{\lambda^2-0.024}$		Conc. 0.7824 *M* (in heptane) $l=40$ cm $[M]^{25}=\frac{1.3482}{\lambda^2-0.025}$		Conc. 0.8885 *M* $l=100$ cm $[M]^{25}=-\frac{0.4167}{\lambda^2-0.023}$		$l=40$ cm $[M]^{25}=-\frac{0.3594}{\lambda^2-0.0288}$	
λ	α^{25}	$[M]^{25}$	α^{25}	$[M]^{25}$	α^{25}	$[M]^{25}$	α^{25}	$[M]^{25}$
5875.6	1.357	3.861	1.260	4.207	−1.150	−1.294	−2.508	−1.132
5780.1	1.412	4.018	1.307	4.364	−1.191	−1.340	−2.608	−1.177
5460.7	1.591	4.527	1.478	4.935	−1.351	−1.520	−2.952	−1.332
4358.3	2.64	7.51	2.45	8.18	−2.22	−2.498	−4.94	−2.23
4046.6	3.14	8.93	2.95	9.85	−2.68	−3.016	−5.86	-2.64_5

columns headed $[M]^{25}_{max}$ have been obtained from the experimental α values multiplied by the ratio

$$\frac{[M]^{25}_{max} \text{ of corresponding halide}}{[M]^{25} \text{ of sample used of corresponding halide}}.$$

These values are minimum values of the maximum molecular rotations. In the case of the secondary azides, where a high degree of racemization is possible, these values should not be considered as representing even the order of magnitude of the maxima rotations.

ABSORPTION SPECTRA

All azides show a characteristic weak absorption band at λ2880. The intensity as well as the position of this band is independent of the nature of the alkyl groups (see Fig. 1). In that respect they differ from the iodides where a slight displacement of the first absorption band was observed between primary and secondary iodides. In fact, intensity and position of the first band in the azides are uninfluenced by the presence in the molecule of phenyl or carboxyl groups. On the contrary, it has been shown that the first absorption band of the iodine atom is different with

TABLE III. *Rotatory dispersion of configurationally primary alkyl azides in heptane.*

	DEXTRO 1-AZIDO-2-METHYLBUTANE $d_4^{25}=0.8770$ (in vacuum) $n_D^{25}=1.4235$. Conc. 0.895 *M* Visible region: $l=40$ cm U.V. region: $l=5$ cm, 0.5 for λ2500 $[M]^{25}_{max}=\frac{3.211}{\lambda^2-0.0362}$		LEVO 1-AZIDO-2-METHYLNONANE $d_4^{25}=0.8658$ (in vacuum), $n_D^{25}=1.4430$ Conc. 0.410 *M* $l=100$ cm $[M]^{25}_{max}=-\frac{0.717}{\lambda^2-0.0043}$		DEXTRO 1-AZIDO-3-METHYLPENTANE $n_D^{25}=1.4300$ Conc. 0.898 *M* Visible region: $l=40$ cm U.V. region: $l=10$ cm $[M]^{25}_{max}=\frac{8.300}{\lambda^2-0.0352}$		DEXTRO 1-AZIDO-4-METHYLHEXANE $d_4^{25}=0.8636$ (in vacuum), $n_D^{25}=1.4324$ Conc. 1.062 *M* $l=40$ cm $[M]^{25}_{max}=\frac{5.340}{\lambda^2-0.0312}$	
λ	α^{25}	$[M]^{25}_{max}$	α^{25}	$[M]^{25}_{max}$	α^{25}	$[M]^{25}_{max}$	α^{25}	$[M]^{25}_{max}$
5875.6	1.863	10.40	—	—	3.460	26.78	2.227	17.05
5780.1	1.932	10.79	−0.324	−2.17	3.587	27.76	2.302	17.63
5460.7	2.195	12.26	−0.363	-2.43_5	4.083	31.60	2.613	20.01
4358.3	3.74_7	20.93	-0.57_5	−3.86	6.935	53.68	4.39_5	33.65
4046.6	4.51	25.19	−0.67	−4.49	8.34	64.56	5.28	40.4
3790	—	—	—	—	2.50	77.4	—	—
3710	—	—	—	—	—	—	1.60 (10 cm)	49.0
3675	—	—	—	—	2.75	85.2	—	—
3580	0.77	34	—	—	—	—	—	—
2500	0.12 conc. 0.358 *M*	130	—	—	—	—	—	—

respect to intensity as well as position in α-iodo-acids as compared with alkyl iodides.[2]

In all the alkyl azides which we have tested—and most probably in all alkyl azides—the rotatory contribution of the band λ2880 is entirely negligible.

Precise dispersion measurements could not be carried out very far into the U.V. region on account of the proximity of the first absorption band. The dispersion of all compounds could be expressed satisfactorily for the wave-length interval covered, by a one term Drude formula.

Azides Having $n_2=0$

In the case of two of the secondary azides, the rotations were sufficiently large to permit measurements on the lower wave-length side of the first band, and it was found that, for that region, departures from the one term formula were small which brings additional evidence to the effect that the contribution of this band is negligible.

The value of the dispersion constant of the secondary azides of the methyl series ($n_2=0$) is very low ($\lambda_0 \simeq 1700$A), if one considers that from λ2200 down, there is a strong absorption region ($\epsilon=380$ at λ2200).

Now that a sufficiently large number of simple organic molecules with one asymmetric carbon atom have been investigated, it becomes more and more evident that when the molecule possesses only one functional group, the first weak absorption bands of the latter are generally weakly or not at all anisotropic (aliphatic aldehydes being an exception). This is contrary to the statement of Kuhn who maintains that the first weak ultraviolet absorption bands practically rule the course of the rotatory power. His statement was based on the fact that most of the substances which he examined had two functional groups attached to the asymmetric carbon atom (halogeno acids or azido acids, for example). It is the presence of the second functional group which renders these weak bands anisotropic.

It was previously found that in a *series of substances with one functional group and homologous with respect to one of the alkyl groups* (R_3 *for instance*), *the sign of the rotatory contribution of the functional group remains the same in the whole series*. It is apparent from Table II that the sign of rotation of 4-azidooctane is opposite to that of the 2-azido- or 3-azido-substituted hydrocarbons (homologous series with respect to R_1), but the constant of dispersion is practically the same for all the derivatives.

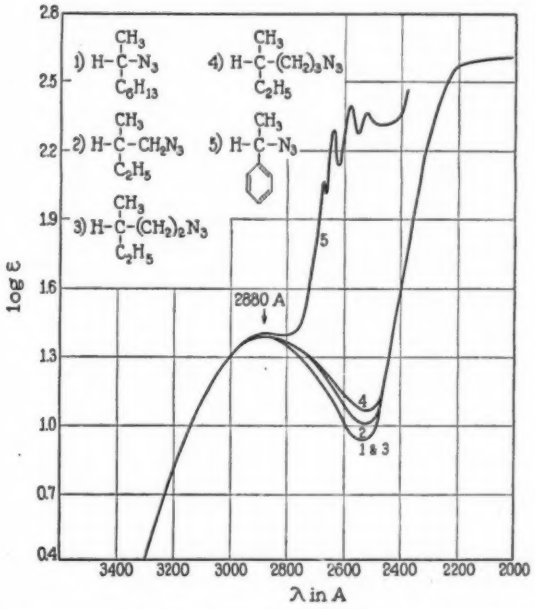

Fig. 1. Absorption curves of alkyl and phenyl azides.

These facts seem to be contradictory to the rule just enunciated. But when one considers the low value of the dispersion constant and the narrow wave-length interval where rotatory measurements could be carried out, one must conclude for the present that it is quite possible that there are in the azides two active absorption regions corresponding to two different electronic states furnishing partial rotations of opposite sign. These active absorption regions may be so closely located as to produce only a very small difference in the course of the rotatory dispersion.

Azides Having $n_2=1$

In the primary azides with $n_2=1$ (see Table III), one observes that the members with $n_3=1$ and $n_3=6$ have rotations opposite in sign. This change of sign is connected with a corresponding change in the rotatory dispersion curve. The dispersion curves of the lower members of the series homologous with respect to n_3 are normal and those of the higher members are anomalous.

[2] P. A. Levene and A. Rothen, J. Biol. Chem. **107**, 533 (1934).

TABLE IV. *Rotatory dispersion of a phenylazide and an azido acid.*

	1-AZIDO-1-PHENYLMETHANE IN HEPTANE $d_4^{25}=1.0321$ (in vacuum), $nD^{25}=1.5233$ Conc. 0.700 *M* Visible region: $l=100$ cm U.V. region: $l=10$ cm $[M]^{25}=\frac{0.4584}{\lambda^2-0.052}$		DEXTRO 2-AZIDOPROPIONIC ACID-1 IN HEPTANE Conc. 0.400 *M* Visible region: $l=40$ cm U.V. region: $l=5$ cm, 0.5 cm for λ3100 $[M]^{25}=-\frac{2.525}{\lambda^2-0.0801}+\frac{4.710}{\lambda^2-0.020}$		LEVO SODIUM* SALT of 2-AZIDOPROPIONIC ACID-1 IN WATER $\alpha=-\frac{1.202}{\lambda^2-0.100}$
λ	α^{25}	$[M]^{25}$	α^{25}	$[M]^{25}$	
5892.6					−4.867
5875.6	21.130	35.627			
5780.1	21.969	37.042	+0.808	+5.05	−5.141
5460.7	25.194	42.480	+0.858	+5.32$_5$	−6.144
4358.3	44.96	75.81	+0.755	+4.72	−13.4
4046.6	55.40	93.41	+0.41	+2.56	
3858	6.37	107.4	—		
3765	6.85	115.5	—		
3710	—	—	—		
3685	7.35	123.9	—		
3610	7.85	132.3	—		
3520			−0.30	−15.0	
3430			−0.40	−20.0	
3320	1.05 (1 cm)	177			
3160			−0.15	−75.0	
3050	0.15 (0.1 cm)	250			
2800	0.25	420			

* The levo sodium salt on which the dispersion measurements were made was obtained from a sample of dextro azidopropionic acid of different rotation from that used for dispersion measurements.

Thus, the direction of the corresponding partial rotations remains the same in all members, but the numerical value of the first contribution is larger in the lower homolog and smaller in the compound with $n_3=6$.

The dispersion constants of the *primary azides with $n_2=2$ or 3* are approximately the same and correspond to $\lambda_0 \backsimeq 1800$A.

Rotatory dispersion data concerning methyl-phenylazido methane and α-azidopropionic acid and its sodium salt are given in Table IV. Inspection of the equation representing the dispersion curve shows that the presence of a phenyl group on the asymmetric carbon atom does not render anisotropic the band λ2880 of the azido group. On the other hand, this band is strongly coupled in the azidopropionic acid. The course of the dispersion of the free acid is anomalous and analogous to that of the methyl-ester investigated by Kuhn *et al.*[3] The sodium salt, on the other hand, is opposite in sign to the free acid or its ester. The dispersion runs a normal course, the partial contribution of the band λ2880 being predominant. The higher value ($\lambda_0^2=0.100$) of the dispersion constant of a one term Drude formula representing the dispersion is due to the fact that the second term is opposite in sign to the first and not much smaller in absolute value.

EXPERIMENTAL

The instruments described in a previous article were used to determine the rotatory dispersion[4] and the same precision is claimed. Care was taken to insure purity of the samples. For each of them, indices of refraction were taken at the beginning and at the end of the last distillation to be certain of the homogeneity of the product.

Since such azides have not been prepared before, it may be interesting to mention here the value obtained for the refraction of the N_3 group. The mean value computed from the Lorentz formula is as follows: $R_D^{25}=9.0$.

[3] W. Kuhn and E. Braun, Zeits. f. physik. Chemie **B8**, 281 (1931).

[4] P. A. Levene, A. Rothen and R. E. Marker, J. Chem. Phys. **1**, 662 (1933).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Plane Fundamental Modes of Vibration of Deuteroethylenes

In the first part of a recent paper, Wu[1] has discussed the "assignment" of the plane vibration frequencies of the three isomeric deuteroethylenes, which had been calculated by Verleysen and the writer.[2] By the "assignment" of a vibration of the isomer, Wu evidently means its correlation to the "corresponding vibration of C_2H_4," the same notation being used for both. Whether such a correlation should always be possible without ambiguity is not examined. The general conclusion reached is that the groups CH_2, CHD, CD_2 markedly preserve their individuality in the vibrations of the CH_4 and CH_2D_2 molecules; this is just why an assignment of the vibrations is possible. The conclusion agrees entirely with previous work on C_2H_4.[3]

It is the purpose of this letter to call attention to papers[4] in which the same results had already been obtained on a completely quantitative basis. A numerical quadratic potential function was computed from the experimental data obtained by Bonner[5] for C_2H_4, giving a quantitative statement for the coupling of the two separate groups in the molecule through the double bond C=C. The potential function was used to compute the vibration frequency spectrum of monodeuteroethylene, agreeing with the experimental values within less than 1.5 percent.[6, 7] Less satisfactory agreement was obtained in the case of di-isomers and of C_2D_4,[8] the largest discrepancy, in a single case, however, being as high as 5.5 percent. The reason for it is to be found in the inherent indeterminacy which remains in the choice of the potential function, if it is determined only by the data from C_2H_4. The new additional experimental data will enable us to remove the indeterminacy and to compute a potential function for all the ethylenes, the accuracy being finally limited by the unknown anharmonicities of the vibrations.

For C_2H_3D, the three $C_2H_2D_2$ and C_2D_4, besides the frequency spectrum, all the plane modes of vibration have been calculated. The drawings visualize well the extent to which the modes of vibration can be considered as internal fundamental vibrations of two nearly independent groups CH_2, CDH or CD_2 in the molecule (eventually coupled with a CC vibration), or, for the lowest frequencies, as rotations of these rigid groups. (A special notation for this kind of vibrations is desirable). There are cases, especially for C_2H_3D, where the notation used by Wu seems to call for a modification.

There is another general way of interpreting the results, that discloses a close connection between the frequency spectrum and the corresponding modes of vibration: the nearer a frequency of C_2H_3D or $C_2H_2D_2$ lies to a frequency of the completely symmetric molecule C_2H_4 or C_2D_4, the more the corresponding mode of vibration resembles the neighboring mode of C_2H_4 or C_2D_4. If the frequency considered lies near two or more frequencies of C_2H_4 or C_2D_4, the corresponding mode of vibration appears as a combination of the neighboring modes of the completely symmetrical molecule. In the application of this rule, only those neighboring modes of C_2H_4 and C_2D_4 are to be considered that possess the symmetry of the mode investigated.

For instance, in the case of C_2H_3D, to the frequency 1579 cm^{-1}, which lies quite near to the isolated frequency 1623 cm^{-1} of C_2H_4 and the similar frequency of C_2D_4, corresponds a mode of vibration which looks highly symmetrical, although the molecule itself is entirely dissymmetrical. In fact, in the total energy of the vibration as much as 91.5 percent is due to component motions that keep the full symmetry of the C_2H_4 molecule. On the other hand, to the 2266 cm^{-1} frequency of the same molecule corresponds a mode which is a mixture in practically equal proportions of the four modes of different symmetry possessed by C_2D_4 in the neighborhood of that frequency.

From a knowledge of the modes of vibration qualitative predictions, which have already proved useful, can be drawn for the intensities and polarizations in the Raman and the infrared spectrum. Fuller discussion, examples and graphical illustrations will be found in the quoted papers.[3, 7]

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Université de Louvain,
Belgium,
September 8, 1937.

[1] Ta-You Wu, J. Chem. Phys. **5**, 392 (1937).
[2] C. Manneback and A. Verleysen, Nature **138**, 367 (1936).
[3] C. Manneback and A. Verleysen, Ann. de Brux. **B56**, 349 (1936); **57**, 31 (1937).
[4] G. B. Sutherland and D. M. Dennison, Proc. Roy. Soc. **A148**, 250 (1935). J. M. Delfosse, Ann. de Brux. **B45**, 114 (1935).
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[8] M. de Hemptinne, J. C. Jungers and J. M. Delfosse, Nature **140**, 323 (1937); G. B. Sutherland, Nature, in press.

The Gaseous Equilibrium of 1,2-Diiodobutane, Butene-1 and Iodine

Of the equilibria between iodine and gaseous olefines only that involving ethylene has been studied previously.[1, 2] From the temperature coefficient of the equilibrium constants the heat of reaction was calculated to be 13.4 ± 0.5 Cal.

It seemed to be worth while to study other equilibria of this type, primarily to determine whether the heats of iodination follow regularities found to apply to the heats of hydrogenation of the olefinic hydrocarbons.[3]

For the present investigation butene-1 was chosen because it happened to be available in a state of high purity and because, by analogy with the hydrogenation processes, it was hoped that the equilibrium would not be so much displaced towards olefine and iodine as to prevent its quantitative study. 1,2-diiodobutane has been prepared by Forbes and Nelson[4] by photoiodination of butene-1 at low temperatures in Freon solution.

The method employed was in most essentials that described by Cuthbertson and Kistiakowsky,[2] but the reaction flask was placed now in a liquid thermostat and instead of an outside pump to mix the gases a long iron-cored sealed glass tube was rolled on the bottom of the 40 cm long and 75 mm wide reaction tube by a pulsating magnetic field. For the determination of iodine the fraction of light absorbed in passage through the length of the reaction flask was measured, but instead of the phototronic cells previously used two vacuum phototubes connected in a differential circuit to the Penick[5] amplifier were employed. This increased the sensitivity of the apparatus so much that a better monochromatized and a geometrically better defined light beam could be used. The stability of the system was improved also. The scale of the rotary Nicol prism was calibrated in terms of the iodine pressure by introducing sealed capillary tubes with weighed amounts of iodine into the evacuated reaction vessel and breaking them magnetically.

The same procedure was employed in the equilibrium determinations and the pressure of iodine was usually followed for about two days, after which time it invariably reached a constant value. Butene was introduced through stopcocks into the evacuated vessel, but the reaction system was sealed off from the stopcocks and from the rest of the apparatus before the iodine tubes were broken. The total pressure was read on a quartz spiral manometer. Thus enough data were available to calculate the equilibrium pressures of all constituents.

Because of condensation of the constituents at lower temperatures and of the too unfavorable position of equilibrium at higher ones, only a small temperature range could be investigated. At 67.1°C five determinations gave $K = 1.36 \pm 0.06$ atmos. and at 80.7°C three determinations gave 2.74 ± 0.08 atmos.

From these data ΔH of the reaction is computed to be -12.0 ± 1.5 Cal., which is to be compared with the corresponding figure for the iodination of ethylene, -13.4 ± 0.5 Cal. Although due to the large experimental errors it is impossible to make a definite statement, the iodination of butene is apparently less exothermic, and this is made probable also by the observation that the free energy change in the reaction is more positive, by about 0.9 Cal. There seems to be, therefore, the same trend as in the heats of hydrogenation, but if we may draw more inferences than are strictly justified by the accuracy of the data, we are inclined to think that the change in the heat of iodination from ethylene to butene-1 is smaller than in the heats of corresponding hydrogenations, which amounts to about 2.5 Cal.

J. E. Cline
G. B. Kistiakowsky

Harvard University,
Cambridge, Massachusetts,
October 16, 1937.

[1] Mooney and Ludlam, Proc. Roy. Soc. Edin. **49**, 160 (1929).
[2] Cuthbertson and Kistiakowsky, J. Chem. Phys. **3**, 631 (1935).
[3] Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **57**, 65, 876 (1935).
[4] Forbes and Nelson, J. Am. Chem. Soc. **59**, 693 (1937).
[5] Penick, Rev. Sci. Inst. **6**, 115 (1935).

Raman Spectrum of Solid H_2S

The Raman spectrum of solid H_2S was studied by the present writers and four Raman lines with $\Delta\nu$ respectively equal to 80 cm^{-1}, 2523 cm^{-1}, 2547 cm^{-1} and 2558 cm^{-1} were reported.[1] Recently Murphy and Vance have repeated the investigation[2] and have failed to observe the lines at 80 cm^{-1} and 2558 cm^{-1}. We want to point out in this connection that the lines 2547 and 2558 cm^{-1} lie very close to each other and these two lines excited by the Hg line 4046A were just resolved by the Fuess glass spectrograph used by us. This spectrograph has a dispersion of about 18A per mm in the region mentioned above. Probably the spectrograph used by Murphy and Vance was unable to resolve these two lines 2547 and 2558 cm^{-1} and that may be the reason why these authors have observed one line having a frequency almost intermediate between those of the two lines observed by us. As regards the line at 80 cm^{-1} it may be pointed out that this line is a broad band and may not be detected with a spectrograph, which cannot produce lines free from coma. The origin of this band is different from that of the other three lines as discussed previously.

As regards the statement of the above authors that they have recorded the anti-Stokes Raman line at 2523 cm^{-1} of solid H_2S in one hour, we want to point out that it is impossible to record this line at the temperature of liquid air (−180°C) whatever be the efficiency of the experimental arrangement. The ratio of the intensity of the anti-Stokes to that of the Stokes line, according to theoretical calculations, is of the order $1 : 10^{18}$. If the anti-Stokes line is recorded in 1 hour, the Stokes line ought to have been recorded in less than 10^{-14}th of a second. Evidently some mistake has been made by the above authors in the assignment of the line.

S. C. Sirkar
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University College of Science,
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Calcutta, India,
October 5, 1937.

[1] S. C. Sirkar, and J. Gupta, Ind. J. Phys. **10**, 227 (1936).
[2] G. M. Murphy, and J. E. Vance, J. Chem. Phys. **5**, 667 (1937).

Revised Calculation of the Translational Fluctuation Effect in Gaseous Dielectrics

Even in gases, the Clausius-Mossotti ratio is not quite independent of density. Hence if one writes

$$\frac{\epsilon-1}{\epsilon+2}V=P_0\left[1+\frac{\lambda P_0}{V}+\omega\left(\frac{P_0}{V}\right)^2+\cdots\right], \quad (1)$$

where P_0 and V are the molar polarization and volume, the correction term $\lambda P_0/V$ can be detected at high pressures. Owing to the close approach of molecules at collisions, the values of λ are much larger than they would be were the atoms uniformly spaced, so that the phenomenon is sometimes called the "translational fluctuation effect." At the end of a previous article,[1] I calculated λ for a classical model of superposed harmonic oscillators and rigid dipoles. For the special case of nonpolar molecules my formula reduced to

$$\lambda P_0=(8\pi L\alpha^2/3a^3)[1+\tfrac{1}{2}\alpha a^{-3}+2\alpha^2a^{-6}+\cdots]. \quad (2)$$

Here α is the polarizability and a is the distance of closest approach. Kirkwood[2] had previously obtained the formula

$$\lambda P_0=(8\pi L\alpha^2/3a^3)(1+A/3bRT), \quad (3)$$

where A and $b=2\pi La^3/3$ are the constants of the equation of state $p=RT/(V-b)-A/V^2$.

Eq. (3) does not agree with the leading member of (2), obtained by disregarding the part of (2) in square brackets. Consequently I stated that I believed Kirkwood's van der Waals correction, i.e. the last factor of (3), was "extraneous," primarily because of the fact that in the way I made my own calculations the polarization forces were already included in the model, so that it would be redundant and erroneous to introduce in addition an inverse sixth power attractive term, as Kirkwood did. However, my criticism of his work was incorrect, as his computations were made in a different way. He points out to me that the van der Waals correction in (3) is really a part of the a^{-9} term of (2) a fact not very clear in his paper. He further notes that if higher terms in the solution of his Eq. (20) are included, then (3) becomes

$$\lambda P_0=(8\pi L\alpha^2/3a^3)(1+\tfrac{1}{2}\alpha a^{-3}+\alpha^2a^{-6}+A/3bRT+\cdots), \quad (4)$$

and that (4) agrees with (2) if one uses the value

$$A=2\pi kTL^2\alpha^2/a^3 \quad (5)$$

of A appropriate to classical harmonic oscillators. Eq. (5) also, of course, applies to quantum-mechanical oscillators if their characteristic frequency ν is small compared with kT/h. In the other limit $h\nu\gg kT$ the quantal value of A is

$$A=\tfrac{1}{2}\pi h\nu\alpha^2L^2/a^3. \quad (6)$$

Now the harmonic model is being used to depict the induced polarization associated with electronic motions, and so (6) rather than (5) should be employed. Also, since ν is large, (6) is considerably greater than (5), and when (6) rather than (5) is substituted, (4) ceases to agree with (2). The question immediately arises as to whether (4) or (2) is then the better approximation. It immediately becomes apparent that I was wrong in supposing that in considering the translational fluctuation effect it is immaterial whether the oscillators are handled in a classical or quantal way, as is the case in so many problems.

To settle the point definitely, I have therefore revised my calculations, treating the oscillators by quantum mechanics. Inasmuch as only the λ correction term in (2) is desired, only two atoms at a time need be considered in the expansion of the partition function, and accurate quantization of a system of two oscillators is possible with dipole-dipole interaction and an applied electric field, since even with these complications the energy remains a quadratic function of the harmonic displacements, permitting the use of normal coordinates. The procedure is described in somewhat simplified form in a paper by London[3] and need not be explained in detail here. London did not have the terms due to the applied field, as he was not considering dielectric constants, but they are handled by a simple shift in origin. Also the calculations can be made to include polar molecules by treating the rotational coordinates by means of classical theory, and regarding them as fixed parameters insofar as they enter in the quantization of the oscillators. These approximations are fully allowable inasmuch as the frequency of end-over-end rotation is small compared both with kT/h and with the oscillator frequency. Not all the spatial averaging given in my previous paper need be repeated, as it is possible to see from the multiplicative way in which the oscillator functions enter, just how the formulas must be modified in going from the classical to quantal case. It is finally found that if $h\nu\gg kT$, then

$$\begin{aligned}\lambda P_0=&(8\pi L\alpha^2/9a^3)(3+2y)(1+\tfrac{1}{4}\Omega a^{-6}+\Omega^2a^{-12}/10+\cdots)\\&+(4\pi La^3/225a^6)(15+10y+y^2)^2\\&\qquad\times(3+y)^{-1}(1+\tfrac{1}{4}\Omega a^{-6}+\cdots)\\&+(4\pi La^4/225a^9)[(15+10y+y^2)(60+60y+8y^2)\\&\qquad\times(3+y)^{-1}-50(3+2y)],\end{aligned} \quad (7)$$

where $y=\mu^2/\alpha kT$ and $\Omega=\frac{3}{4}h\nu\alpha^2/kT$. The expression $\frac{3}{4}kT\pi L^2\Omega$ is the same as the van der Waals constant A if the molecule is nonpolar and if in addition squares and higher powers of Ω are overlooked. These conditions are basic both to (5) and (6), which alike neglect the effect of the permanent dipole moment μ and cubes of α. If these conditions are met, Eq. (7) is valid for all values of the ratio $h\nu/kT$ if Ω is defined as $3A/2\pi L^2kT$. In (7), all terms in a^{-9} have been included, and also, unless y is very large probably the most important terms in a^{-12} and a^{-15}. For the special case $y=0$ of nonpolar molecules, (7) reduces, except for higher members, to (4). Thus Kirkwood's results are entirely correct, but formula (7) is, of course, more general, in that it includes polar molecules.

Unfortunately use of (7) rather than my former Eq. (20) makes the agreement with experiment worse in the case of NH_3. Namely, the computed value of λ (with London's[3] estimate of ν) becomes about 0.7 rather than 0.4, whereas the observations of Keyes and collaborators give $\lambda=0.3$.

The considerations of the present note in no way affect the discussion of liquids and solids which constituted all but the final section of my previous article. The coefficient of a^{-9} was not involved, and so no distinction between classical and quantal results came into play.

Princeton University,
Princeton, N. J.,
November 11, 1937.

J. H. Van Vleck

[1] J. H. Van Vleck, J. Chem. Phys. **5**, 556 (1937).
[2] J. G. Kirkwood, J. Chem. Phys. **4**, 592 (1936).
[3] F. London, Zeits. f. physik. Chemie **11B**, 222 (1930); Trans. Faraday Soc. **33**, 8 (1937).

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Revised Calculation of the Translational Fluctuation Effect in Gaseous Dielectrics

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$$\frac{\epsilon-1}{\epsilon+2}V=P_0\left[1+\frac{\lambda P_0}{V}+\omega\left(\frac{P_0}{V}\right)^2+\cdots\right], \qquad (1)$$

where P_0 and V are the molar polarization and volume, the correction term $\lambda P_0/V$ can be detected at high pressures. Owing to the close approach of molecules at collisions, the values of λ are much larger than they would be were the atoms uniformly spaced, so that the phenomenon is sometimes called the "translational fluctuation effect." At the end of a previous article,[1] I calculated λ for a classical model of superposed harmonic oscillators and rigid dipoles. For the special case of nonpolar molecules my formula reduced to

$$\lambda P_0=(8\pi L\alpha^2/3a^3)[1+\tfrac{1}{2}\alpha a^{-3}+2\alpha^2a^{-6}+\cdots]. \qquad (2)$$

Here α is the polarizability and a is the distance of closest approach. Kirkwood[2] had previously obtained the formula

$$\lambda P_0=(8\pi L\alpha^2/3a^3)(1+A/3bRT), \qquad (3)$$

where A and $b=2\pi La^3/3$ are the constants of the equation of state $p=RT/(V-b)-A/V^2$.

Eq. (3) does not agree with the leading member of (2), obtained by disregarding the part of (2) in square brackets. Consequently I stated that I believed Kirkwood's van der Waals correction, i.e. the last factor of (3), was "extraneous," primarily because of the fact that in the way I made my own calculations the polarization forces were already included in the model, so that it would be redundant and erroneous to introduce in addition an inverse sixth power attractive term, as Kirkwood did. However, my criticism of his work was incorrect, as his computations were made in a different way. He points out to me that the van der Waals correction in (3) is really a part of the a^{-9} term of (2) a fact not very clear in his paper. He further notes that if higher terms in the solution of his Eq. (20) are included, then (3) becomes

$$\lambda P_0=(8\pi L\alpha^2/3a^3)(1+\tfrac{1}{2}\alpha a^{-3}+\alpha^2a^{-6}+A/3bRT+\cdots), \qquad (4)$$

and that (4) agrees with (2) if one uses the value

$$A=2\pi kTL^2\alpha^2/a^3 \qquad (5)$$

of A appropriate to classical harmonic oscillators. Eq. (5) also, of course, applies to quantum-mechanical oscillators if their characteristic frequency ν is small compared with kT/h. In the other limit $h\nu\gg kT$ the quantal value of A is

$$A=\tfrac{1}{2}\pi h\nu\alpha^2L^2/a^3. \qquad (6)$$

Now the harmonic model is being used to depict the induced polarization associated with electronic motions, and so (6) rather than (5) should be employed. Also, since ν is large, (6) is considerably greater than (5), and when (6) rather than (5) is substituted, (4) ceases to agree with (2). The question immediately arises as to whether (4) or (2) is then the better approximation. It immediately becomes apparent that I was wrong in supposing that in considering the translational fluctuation effect it is immaterial whether the oscillators are handled in a classical or quantal way, as is the case in so many problems.

To settle the point definitely, I have therefore revised my calculations, treating the oscillators by quantum mechanics. Inasmuch as only the λ correction term in (2) is desired, only two atoms at a time need be considered in the expansion of the partition function, and accurate quantization of a system of two oscillators is possible with dipole-dipole interaction and an applied electric field, since even with these complications the energy remains a quadratic function of the harmonic displacements, permitting the use of normal coordinates. The procedure is described in somewhat simplified form in a paper by London[3] and need not be explained in detail here. London did not have the terms due to the applied field, as he was not considering dielectric constants, but they are handled by a simple shift in origin. Also the calculations can be made to include polar molecules by treating the rotational coordinates by means of classical theory, and regarding them as fixed parameters insofar as they enter in the quantization of the oscillators. These approximations are fully allowable inasmuch as the frequency of end-over-end rotation is small compared both with kT/h and with the oscillator frequency. Not all the spatial averaging given in my previous paper need be repeated, as it is possible to see from the multiplicative way in which the oscillator functions enter, just how the formulas must be modified in going from the classical to quantal case. It is finally found that if $h\nu\gg kT$, then

$$\begin{aligned}\lambda P_0=&(8\pi L\alpha^2/9a^3)(3+2y)(1+\tfrac{1}{3}\Omega a^{-6}+\Omega^2a^{-12}/10+\cdots)\\&+(4\pi L\alpha^3/225a^6)(15+10y+y^2)^2\\&\qquad\times(3+y)^{-1}(1+\tfrac{1}{2}\Omega a^{-6}+\cdots)\\&+(4\pi L\alpha^4/225a^9)[(15+10y+y^2)(60+60y+8y^2)\\&\qquad\times(3+y)^{-1}-50(3+2y)],\end{aligned} \qquad (7)$$

where $y=\mu^2/\alpha kT$ and $\Omega=\frac{3}{4}h\nu\alpha^2/kT$. The expression $\frac{2}{3}kT\pi L^2\Omega$ is the same as the van der Waals constant A if the molecule is nonpolar and if in addition squares and higher powers of Ω are overlooked. These conditions are basic both to (5) and (6), which alike neglect the effect of the permanent dipole moment μ and cubes of α. If these conditions are met, Eq. (7) is valid for all values of the ratio $h\nu/kT$ if Ω is defined as $3A/2\pi L^2kT$. In (7), all terms in a^{-9} have been included, and also, unless y is very large probably the most important terms in a^{-12} and a^{-15}. For the special case $y=0$ of nonpolar molecules, (7) reduces, except for higher members, to (4). Thus Kirkwood's results are entirely correct, but formula (7) is, of course, more general, in that it includes polar molecules.

Unfortunately use of (7) rather than my former Eq. (20) makes the agreement with experiment worse in the case of NH_3. Namely, the computed value of λ (with London's[3] estimate of ν) becomes about 0.7 rather than 0.4, whereas the observations of Keyes and collaborators give $\lambda=0.3$.

The considerations of the present note in no way affect the discussion of liquids and solids which constituted all but the final section of my previous article. The coefficient of a^{-9} was not involved, and so no distinction between classical and quantal results came into play.

Princeton University,
Princeton, N. J.,
November 11, 1937.

J. H. VAN VLECK

[1] J. H. Van Vleck, J. Chem. Phys. **5**, 556 (1937).
[2] J. G. Kirkwood, J. Chem. Phys. **4**, 592 (1936).
[3] F. London, Zeits. f. physik. Chemie **11B**, 222 (1930); Trans. Faraday Soc. **33**, 8 (1937).

The Infrared Association Band of a Heavy Alcohol

By comparing the infrared absorption spectra of different alcohols in the region of the fundamental O—H vibration in gaseous and liquid state it is possible to draw some conclusions about the association. Several workers have studied these association bands, most in the region of the harmonics. Errera and Mollet[1] found for solutions of C_2H_5OH in CCl_4 two bands, one at 3640 cm^{-1} (2.73μ) and a broad band at about 3350 cm^{-1} (3μ). The first is ascribed to the monomolecules and the second to intermolecular O—H vibrations. The temperature effect is in accord with this supposition, for increasing the temperature decreases the intensity of the broad intermolecular band and at the same time increases that of the monomolecular band. As was expected the vapor state shows a sharp monomolecular band. The methyl band at 3.4μ is not shifted.

We were able to find an analogous effect for water by comparing the absorption in the gaseous, liquid and solid states, and in solutions of water in CCl_4, CS_2 or dioxane.[2] Many suggestions have been given as to the interpretation of these association bands.[3] It is however not yet possible to draw any definite conclusions about the character of these complexes from infrared data.

The isotope effect has proved to be very helpful in the explanation of differents bands. In studying the fine-structure of one of the heavy alcohols we found the same effect as described above. The methylband (in this case CH_2D of the molecule CH_2DOD) remains in the same place for the gaseous and the liquid state. The monomolecular band at 2721 cm^{-1} disappears in the liquid state (only a small inflection is to be seen) and a broad association band is found at about 2500 cm^{-1}. These data are obtained with a prism grating instrument. The transmission curve is composed of three parts due to the changing of the fore-prism. The methyl band in the spectrum of the vapor state was measured by lowering the pressure of the alcohol vapor.

The O—D band at 2721 cm^{-1} proved to have the features of a parallel band and has a fine structure with a sharp zero branch. These results will be published later.

Bartholomé and Sachsse[4] measured the spectrum of CH_3OH and CH_3OD only with prisms of CaF_2 and NaCl. They found a methyl band at 3000 cm^{-1} and the O—H and O—D stretching vibrations respectively at 3400 and 2420 cm^{-1}. These data do not agree with the results of Errera and Mollet, nor with our measurements. We must suppose that in their cell a small amount of alcohol is condensed on the windows. This is very possible for a very thin layer of alcohol (only a few drops between two polished plates of KBr of 5 cm^2 surface) gave us the association band as Fig. 1 shows. The O—D band moreover is rather sharp and it was studied by these authors with the fluorite prism which has a very small dispersion in this region.

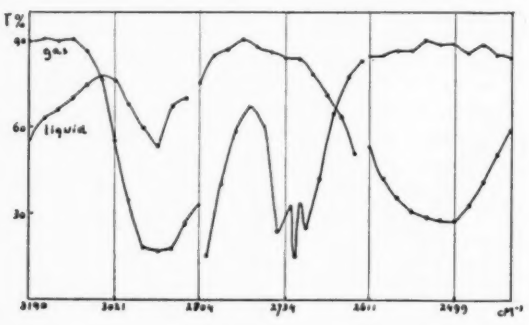

FIG. 1. The transmission curve of CH_2DOD in the gaseous and liquid state.

Also, the Raman spectra have been studied recently by Halford, Anderson and Kissin.[5] They find the methyl bands at 2890 cm^{-1} and 2987 cm^{-1} (we also resolved the methyl band at 2900 cm^{-1}) and ascribe the broad band at 3400 cm^{-1} to the O—H stretching motion and the smaller band at 2500 cm^{-1} to the O—D stretching motion. Also in this case it is our opinion that these bands are due to association since their observations were carried out in the liquid state.

We thank Professor L. C. Anderson of the department of chemistry for permitting us to use a sample of the heavy alcohol and Professor E. F. Barker for his kind interest.

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Leiden,
November 13, 1937.

[1] J. Errera and P. Mollet, Nature **138**, 882 (1936); Trans. Faraday Soc. **33**, 122 (1937); Comptes rendus **204**, 259 (1937).
[2] G. Bosschieter and J. Errera, J. de physique **8**, 229 (1937) and Comptes rendus **204**, 1719 (1937); **205**, 560 (1937).
[3] R. M. Badger and S. H. Bauer, J. Chem. Phys. **5**, 839 (1937).
[4] E. Bartholomé and H. Sachsse, Zeits. f. physik. Chemie **B30**, 40 (1935).
[5] J. O. Halford, L. C. Anderson, G. H. Kissin, J. Chem. Phys. **5**, 927 (1937).

The Raman Spectra of CH_3CF_3 and CCl_2CF_2*

Because of the interest attached to ethane and ethane-like molecules in connection with the question of free rotation of the CX_3 groups with respect to each other, it was considered that the Raman spectrum of CH_3CF_3 might yield additional information on this point. Inasmuch as the spectrum of the liquid can be conveniently photographed only at low temperatures (b.p. about −40°), the determination of the polarization of the scattered light would be experimentally very difficult and was not attempted. The fact that the frequencies associated with the CF_3 group will be considerably different in magnitude from those of the CH_3 group may, in the analysis, compensate for the lack of data on polarization. Only the results of the experiments are presented here; the assignment of the frequencies will be given when completed. The Raman spectrum of the ethylene-like molecule $CCl_2=CF_2$ was photographed at room temperature with the substance in the liquid state, and the observed shifts are presented here.

The compounds were kindly furnished us by Dr. A. L. Henne in a pure or nearly pure state to begin with, and they were further fractionally distilled before placing them in the Pyrex or quartz Raman tubes. Spectra of CH_3CF_3 gas and liquid, and CF_2CCl_2 liquid were photographed,

TABLE I. *The Raman spectrum of CH_3CF_3 liquid at −75°.*

Frequency in cm^{-1}	Character	Number of Exciting Lines Scattered from
358 (2)		2
541 (2)	Sharp	3
603 (2)	Sharp	2
829 (5)	Sharp	5
968 (3)		3
1279 (1)		1
1450 (4)	Diffuse	2
2792 (2)		1
2825 (1)		2
2885 (1) ?	Diffuse	1
2974 (5)		8
3040 (4)	Diffuse	5

TABLE II. *The Raman spectrum of $CF_2=CCl_2$ liquid at room temperature.*

Frequency in cm^{-1}	Character	Number of Exciting Lines Scattered from
255 (6)		7
435 (7)	Sharp	4
454 (1)		2
562 (6)		5
622 (4)	Sharp	5
648 (2)	Diffuse	2
883 ($\frac{1}{2}$)	Diffuse	1
1027 (2)	Diffuse	2
1123 (1)		2
1735 (6)		2
1976 ($\frac{1}{2}$)	Diffuse	2

the exposure times varying from one to twenty hours in the case of the liquids. A quinine hydrochloride solution filter between the mercury arc and the tube was used in some exposures on both compounds to determine which of the observed lines were excited by 4358A and which by 4078 or 4047A. This test or an equivalent one is necessary for those cases in which the scattered lines from two or more exciting lines overlap. In Table I the numbers in parentheses adjoining the frequency values indicate estimated relative intensities.

Since CH_3CF_3 gas absorbs fairly strongly in the ultraviolet, the results of experiments on it are not presented separately, and they were of use only in confirming the 3040, 2974 and 829 cm^{-1} lines. The absorption resulted in the photochemical decomposition of the gas. The substance in the liquid form is colorless and showed no absorption in the visible region.

The selection rules[1] for CH_3CF_3, assuming a symmetry of C_{3v}, permit a total of 11 fundamental frequencies in the Raman spectrum, of which 6 would have a polarization $\rho=\frac{3}{4}$. Twelve lines in all were observed, of which the one with a frequency of 2885 cm^{-1} is the only doubtful one. For purposes of comparison it is of interest to set down here the vibrational frequencies obtained for CF_4 in the Raman spectrum[2] and infrared;[3] $\nu_1(1)$, 904; $\nu_2(2)$, 437; $\nu_3(3)$, 1252; $\nu_4(3)$, 635 cm^{-1}. The selection rules for $CF_2=CCl_2$ permit 12 fundamental frequencies to appear in the Raman spectrum (7 with $\rho=\frac{3}{4}$) if the symmetry is assumed to be C_{2v}, while only 11 were observed. Moreover some of the weaker lines may be combinations of overtones.

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California Institute of Technology,
Pasadena, California,
October 27, 1937.

* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 630.

[1] The selection rules for the CH_3CF_3 type molecule were determined by Dr. Fred Stitt.

[2] Yost, Lassettre and Gross, J. Chem. Phys. **4**, 325 (1936).

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The Separation of Mixtures by Centrifuging

The separation of a mixture into its pure constituents by the usual methods such as fractional distillation, fractional crystallization, etc., sometimes is a very slow and tedious process. This is especially true in the case of many constant boiling point mixtures. Therefore, it might be of interest to mention some experiments in which our vacuum type tubular centrifuge was used to separate a mixture of substances of different molecular weights while in the vapor state.

Briefly, the centrifuge consists of a vacuum tight alloy steel tube 2.6 cm (effective) internal diameter and 12.5 cm long, which spins inside a vacuum chamber.[1] The vapor entered the spinning tube at the top through a stainless steel hypodermic needle tube (gauge 15), and the lighter and heavier fractions were collected at the bottom through two coaxial stainless steel hypodermic needle tubes (gauges 15 and 12), communicating with the axis of rotation and the periphery of the spinning tube, respectively. The inlet to the spinning tube was sealed (by vacuum tight oil glands) to a flask containing a mixture (constant boiling point) of carbon tetrachloride and methyl alcohol, and the outlets which collected the lighter and heavier fractions were sealed, also by vacuum tight oil glands, each to a separate trap immersed in dry ice. The system was evacuated and the vapor passed through the centrifuge at the rate of approximately a cubic centimeter of liquid per minute. In each experiment precaution was taken to make sure that practically all of the mixture placed in the flask passed through the centrifuge and was collected in the dry-ice traps; also, that approximately equal light and heavy fractions were collected. Care was taken to insure that each fraction contained only the carbon tetrachloride—methyl alcohol mixture and hence was free of possible impurities such as vacuum pump oil, etc. With the tube or centrifuge spinning 1800 r.p.s. the density of the heavier fraction in the liquid state was roughly 4.7 percent heavier than that of the lighter fraction in the liquid state at the same temperature.

According to the well-known theory for the centrifuging of gases[2] when equilibrium is established

$$K_p/K_p' = e^{(M_1-M_2)w^2r^2/2RT}$$

where M_1 and M_2 are the molecular weights of the two gases, respectively, T the absolute temperature, R the gas constant, r the radius of the centrifuge, w the angular velocity in radians per sec., K_p the ratio of the quantities

of heavy substance to light substance at the periphery of the rotor, and K_c the ratio of the quantities of the heavy to the light substances at the center of the centrifuge. This equation has been shown to be in agreement with experiment[2] for gases which approximately obey Boyle's law. If it is assumed to hold in the experiment described above, then K_p/K_c comes out 1.7 and the density should have changed by about 5.7 percent, which is within 20 percent of the above experimental value. Therefore, the theory of separation apparently can be depended upon to give at least the right order of magnitude for the separation of a mixture of vapors.

It is interesting to observe that K_p/K_c increases very rapidly with wr or the peripheral velocity of the rotor. With the tubular or other vacuum type centrifuges the only factor which limits the maximum angular velocity, or the wr attainable is the bursting strength of the spinning tube or centrifuge. We have worked with hollow rotors with an effective wr of 5×10^4 cm/sec. and it is probable that with the proper material and construction of rotor that a wr of 6 or 7×10^4 cm/sec. might be obtained. However, assuming only the 5×10^4 cm/sec., $K_p/K_c=446$ for the methyl alcohol-carbon tetrachloride mixture. Consequently the lighter fraction would become almost pure methyl alcohol and the heavier fraction almost pure carbon tetrachloride in a single centrifuging. Obviously by drawing off a smaller amount of the substance to be concentrated, greater purification can be obtained. It is also possible to design a multistage centrifuge which should greatly increase the concentration as well as the speed with which the centrifuging takes place. Therefore centrifuging might become a useful supplement to fractional distillation for the separation of some substances that have different molecular weights.

We are greatly indebted to the Natural Science Division of the Rockefeller Foundation for a grant which has made possible the development of the tubular vacuum type centrifuge.

J. W. Beams
L. B. Snoddy

Rouss Physical Laboratory,
University of Virginia,
November 5, 1937.

[1] For a description and drawings of the centrifuge see Beams, Linke and Skarstrom, Science **86**, 293 (1937), Figs. 1 and 2.
[2] Lindemann and Aston, Phil. Mag. **37**, 530 (1919). Aston, *Isotopes* (Longmans, Green and Co., 1924). Mulliken, J. Am. Chem. Soc. **44**, 1033 (1922); **45**, 1592 (1923).
[3] Beams and Haynes, Phys. Rev. **50**, 149 (1936).

Low and High Raman Frequencies for Water

In a recent note[1] I. R. Rao and P. Koteswaram state that some of the Raman bands for water reported by other workers do not correspond to different frequencies of water excited by the λ2537 mercury line but are ascribable to the $\Delta\tilde{\nu}$3200–3600 band of water excited by lines other than the λ2537 line. The bands at $\Delta\tilde{\nu}$500 and 2150 reported by the writer[2] were ascribed by Rao and Koteswaram to the mercury exciting line λ2464, and $\Delta\tilde{\nu}$175 to λ2345.

The writer assigned the frequencies $\Delta\tilde{\nu}$175, 500 and 2150 to the λ2537 mercury line as the source of excitation for the reason that in the type of mercury lamp employed by him in these experiments, namely "Sc 2537,"[3] there is no line at a wave-length less than λ2537 capable of giving rise to any Raman frequency, hence multiple excitation does not exist. The intensity of the mercury lines λ2345, 2378 and 2464 is less than 1 percent (probably nearer 0.1 percent) of λ2537 in this type of low pressure mercury discharge tube. It is probable that Rao and Koteswaram are not familiar with this lamp. In the ordinary type of mercury burner the lines λ2345, 2378 and 2464 might be sufficiently intense to cause multiple excitation. In the low pressure arc 85 percent of the total energy output of the lamp is confined to the λ2537 line, and because of the low mercury pressure there is no reversal effect. In consequence of this there is an even greater difference between the intensity of the λ2537 line and other mercury lines.

However, to eliminate any possible doubt in the matter, the Raman spectrum of water was redetermined, using an acetic acid and sodium acetate filter between the mercury arc and the Raman tube. This completely absorbed all radiation of a wave-length less than λ2537. There was no change in the Raman spectrum of water, and the bands at $\Delta\tilde{\nu}$175, 500, 1659 and 2150, etc. appeared as previously described.

So far as the frequencies $\Delta\tilde{\nu}$4023 and 5100 are concerned, these have been reported by other workers and have not been observed by the writer. Rao and Koteswaram ascribe these shifts to an excitation by λ2576 and 2652 respectively, yielding therefore $\Delta\tilde{\nu}$3414 and 3383 instead of $\Delta\tilde{\nu}$4023 and 5100. However, no multiple excitation by the mercury lines λ2576 and 2562 has been observed during the study of many organic compounds. If these were the source of multiple excitation, duplicate lines would have appeared in these studies. It is probable, therefore, that difference in types of lamps may make inapplicable the conclusions of Rao and Koteswaram insofar as they apply to the low mercury pressure source of illumination.

James H. Hibben

Geophysical Laboratory,
Carnegie Institution of Washington,
November 8, 1937.

[1] J. Chem. Phys. **5**, 667 (1937).
[2] J. Chem. Phys. **5**, 166 (1937).
[3] Hanovia Chemical Mfg. Co., Newark, N. J.

Corrections to: A Method for Deriving Expressions for the First Partial Derivatives of Thermodynamic Functions.

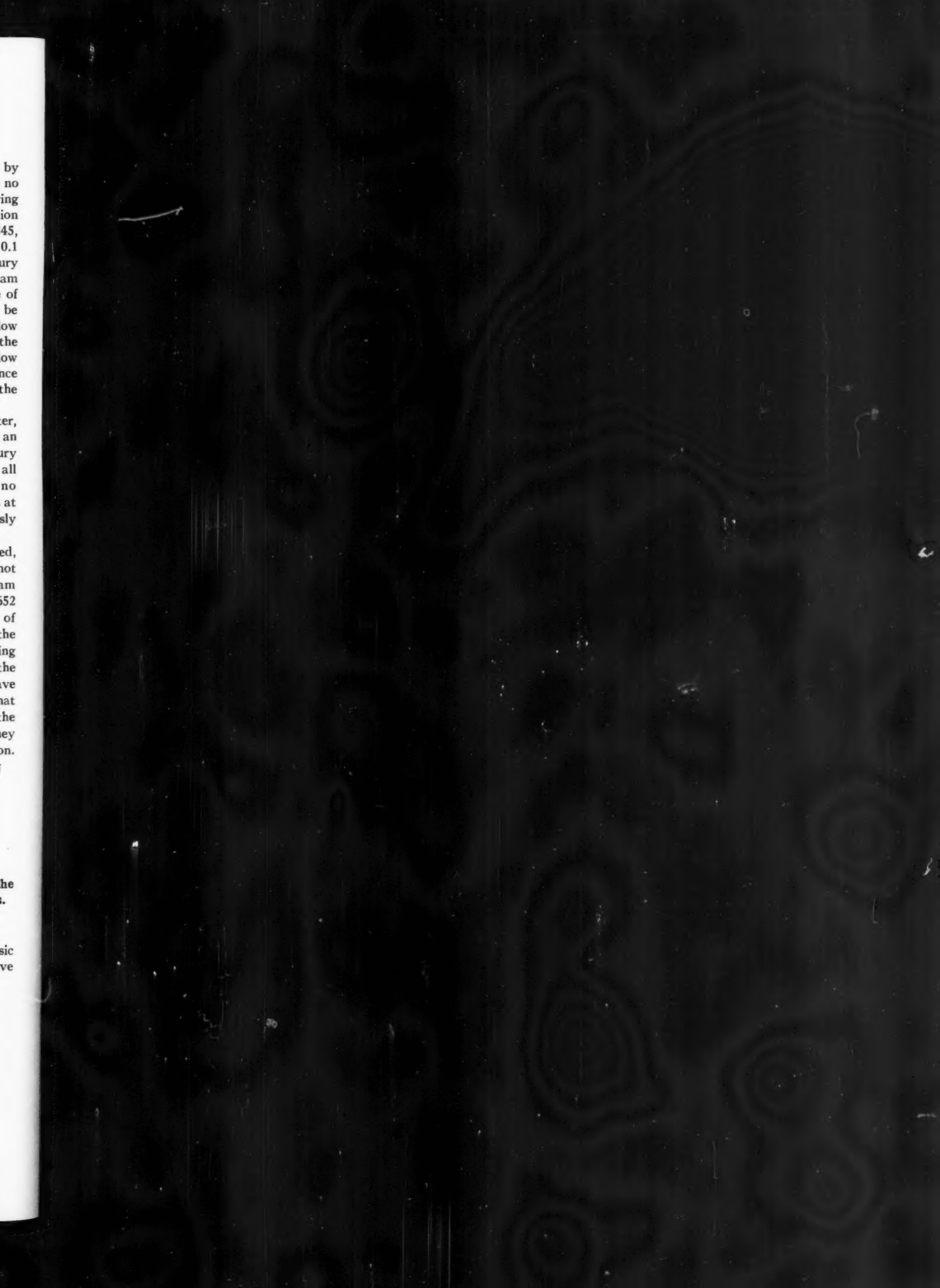
(J. Chem. Phys. **5**, 792 (1937))

The symbols C_P and C_V in the equations for basic vireds at the bottom of the first column, page 793, have been interchanged. The corrected equations are:

$$dT_P=1=T/C_P dS_P,$$
$$dT_V=(\partial V/\partial P)_T=T/C_V dS_V,$$
$$dV_P=(\partial V/\partial T)_P=dS_T.$$

Frank Lerman

Department of Chemistry,
University of Cincinnati,
Cincinnati, Ohio,
October 27, 1937.



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